

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> : <b>C08F 210/16, 110/02, 110/06, 210/06, 210/14, 210/16, 4/60, C08L 23/16</b>		<b>A2</b>	(11) International Publication Number: <b>WO 96/23010</b>
(21) International Application Number: <b>PCT/US96/01282</b>		(43) International Publication Date: <b>1 August 1996 (01.08.96)</b>	
(22) International Filing Date: <b>24 January 1996 (24.01.96)</b>		(72) Inventors: <b>JOHNSON, Lynda, Kaye; Apartment 5B2, 402 Foulk Road, Wilmington, DE 19803-3805 (US). KILLIAN, Christopher, Moore; 406 Summerwalk Circle, Chapel Hill, NC 27514 (US). ARTHUR, Samuel, David; 3214 North Monroe Street, Wilmington, DE 19802-2654 (US). FELD-MAN, Jerald; 16 Cinnamon Drive, Hockessin, DE 19707-1349 (US). McCORD, Elizabeth, Forrester; 514 Hemlock Drive, Hockessin, DE 19707-9361 (US). McLAIN, Stephan, James; 202 Old Mill Lane, Wilmington, DE 19803-4922 (US). KREUTZER, Kristina, Ann; Apartment 2C, 4 Doe Run Court, Wilmington, DE 19808-2059 (US). BEN-NETT, Margaret, Anne; 1 Brandywine Falls, Wilmington, DE 19806 (US). COUGHLIN, Edward, Bryan; Apartment E, 2227 Prior Road, Wilmington, DE 19809 (US). ITTEL, Steven, Dale; 2802 Landon Drive, Wilmington, DE 19810-2213 (US). PARTHASARATHY, Anju; 1562 Pottstown Pike, Glenmoore, PA 19343-9614 (US). TEMPEL, Daniel, Joseph; Apartment 10, 400 Davie Road, Carrboro, NC 27510 (US). BROOKHART, Maurice, S.; 944 Old Orchard Road, Chapel Hill, NC 27514 (US).</b>	
(30) Priority Data: 08/378,044      24 January 1995 (24.01.95)      US 08/415,283      3 April 1995 (03.04.95)      US 08/473,590      7 June 1995 (07.06.95)      US 60/007,375      8 August 1995 (08.08.95)      US 60/002,654      22 August 1995 (22.08.95)      US		(74) Agents: <b>EVANS, Craig, H. et al.; E.I. du Pont de Nemours and Company, Legal Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).</b>	
(71) Applicants: <b>E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). UNIVERSITY OF NORTH CAROLINA AT CHAPEL HILL [US/US]; Office of Technology Development, Campus Box 4105, 308 Bynum Hall, Chapel Hill, NC 27599-4105 (US).</b>		(81) Designated States: <b>AL, AM, AU, BB, BG, BR, CA, CN, CZ, EE, FI, GE, HU, IS, JP, KP, KR, LK, LR, LT, LV, MD, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, TR, TT, UA, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AZ, BY, KG, KZ, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</b>	
<b>Published</b> <i>Without international search report and to be republished upon receipt of that report.</i>			
(54) Title: <b><math>\alpha</math>-OLEFINS AND OLEFIN POLYMERS AND PROCESSES THEREFOR</b>			
(57) Abstract <p>Disclosed herein are processes for polymerizing ethylene, acyclic olefins, and/or selected cyclic olefins, and optionally selected olefinic esters or carboxylic acids, and other monomers. The polymerizations are catalysed by selected transition metal compounds, and sometimes other co-catalysts. Since some of the polymerizations exhibit some characteristics of living polymerizations, block copolymers can be readily made. Many of the polymers produced are often novel, particularly in regard to their microstructure, which gives some of them unusual properties. Numerous novel catalysts are disclosed, as well as some novel processes for making them. The polymers made are useful as elastomers, molding resins, in adhesives, etc. Also described herein is the synthesis of linear <math>\alpha</math>-olefins by the oligomerization of ethylene using as a catalyst system a combination of a nickel compound having a selected <math>\alpha</math>-diimine ligand and a selected Lewis or Bronsted acid, or by contacting selected <math>\delta</math>(<math>\alpha</math>)-diimine nickel complexes with ethylene.</p>			

**BEST AVAILABLE COPY**

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

**TITLE**

$\alpha$ -OLEFINS AND OLEFIN POLYMERS AND PROCESSES THEREFOR

This application is a continuation-in-part of pending prior application Serial No. 60/002,654, filed August 22, 1995, is also a continuation-in-part of pending application Serial No. 60/007,375, filed August 8, 1995, is also a continuation-in-part of pending application Serial No. 08/473,590, filed June 7, 1995, which is a continuation-in-part of prior pending application Serial No. 08/415,283, filed April 3, 1995, which is a continuation-in-part of pending prior application Serial No. 08/378,044 filed January 24, 1995.

**FIELD OF THE INVENTION**

The invention concerns novel homo- and copolymers of ethylene and/or one or more acyclic olefins, and/or selected cyclic olefins, and optionally selected ester, carboxylic acid, or other functional group containing olefins as comonomers; selected transition metal containing polymerization catalysts; and processes for making such polymers, intermediates for such catalysts, and new processes for making such catalysts. Also disclosed herein is a process for the production of linear alpha-olefins by contacting ethylene with a nickel compound of the formula  $[DAB]NiX$ , wherein DAB is a selected  $\alpha$ -diimine and X is chlorine, bromine, iodine or alkyl, and a selected Lewis or Bronsted acid, or by contacting ethylene with other selected  $\alpha$ -diimine nickel complexes

**BACKGROUND OF THE INVENTION**

Homo- and copolymers of ethylene (E) and/or one or more acyclic olefins, and/or cyclic olefins, and/or substituted olefins, and optionally selected olefinic esters or carboxylic acids; and other types of monomers, are useful materials, being used as plastics for packaging materials, molded items, films, etc., and as elastomers for molded goods, belts of various types, in tires, adhesives, and for other uses. It is well

known in the art that the structure of these various polymers, and hence their properties and uses, are highly dependent on the catalyst and specific conditions used during their synthesis. In addition to  
5 these factors, processes in which these types of polymers can be made at reduced cost are also important. Therefore, improved processes for making such (new) polymers are of interest. Also disclosed herein are uses for the novel polymers.

10  $\alpha$ -Olefins are commercial materials being particularly useful as monomers and as chemical intermediates. For a review of  $\alpha$ -olefins, including their uses and preparation, see B. Elvers, et al., Ed.,  
15 Ullmann's Encyclopedia of Industrial Chemistry, 5th Ed., Vol. A13, VCH Verlagsgesellschaft mbH, Weinheim, 1989, p. 238-251. They are useful as chemical intermediates and they are often made by the oligomerization of ethylene using various types of  
20 catalysts. Therefore catalysts which are capable of forming  $\alpha$ -olefins from ethylene are constantly sought.

#### SUMMARY OF THE INVENTION

This invention concerns a polyolefin, which contains about 80 to about 150 branches per 1000 methylene groups, and which contains for every 100  
25 branches that are methyl, about 30 to about 90 ethyl branches, about 4 to about 20 propyl branches, about 15 to about 50 butyl branches, about 3 to about 15 amyl branches, and about 30 to about 140 hexyl or longer branches.

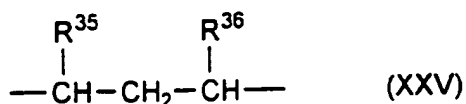
30 This invention also concerns a polyolefin which contains about 20 to about 150 branches per 1000 methylene groups, and which contains for every 100 branches that are methyl, about 4 to about 20 ethyl branches, about 1 to about 12 propyl branches, about 1  
35 to about 12 butyl branches, about 1 to about 10 amyl branches, and 0 to about 20 hexyl or longer branches.

Disclosed herein is a polymer, consisting essentially of repeat units derived from the monomers,



ethylene and a compound of the formula  
 $\text{CH}_2=\text{CH}(\text{CH}_2)_m\text{CO}_2\text{R}^1$ , wherein  $\text{R}^1$  is hydrogen, hydrocarbyl or  
 substituted hydrocarbyl, and  $m$  is 0 or an integer from  
 1 to 16, and which contains about 0.01 to about 40 mole  
 5 percent of repeat units derived from said compound, and  
 provided that said repeat units derived from said  
 compound are in branches of the formula  $-\text{CH}(\text{CH}_2)_n\text{CO}_2\text{R}^1$ ,  
 in about 30 to about 70 mole percent of said branches  $n$   
 is 5 or more, in about 0 to about 20 mole percent  $n$  is  
 10 4, in about 3 to 60 mole percent  $n$  is 1, 2 and 3, and  
 in about 1 to about 60 mole percent  $n$  is 0.

This invention concerns a polymer of one or more  
 alpha-olefins of the formula  $\text{CH}_2=\text{CH}(\text{CH}_2)_a\text{H}$  wherein  $a$  is  
 an integer of 2 or more, which contains the structure  
 15 (XXV)

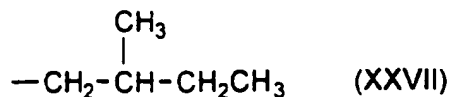


wherein  $\text{R}^{35}$  is an alkyl group and  $\text{R}^{36}$  is an alkyl group  
 20 containing two or more carbon atoms, and provided that  
 $\text{R}^{35}$  is methyl in about 2 mole percent or more of the  
 total amount of (XXV) in said polymer.

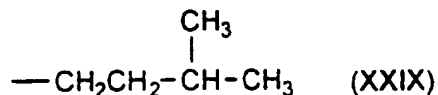
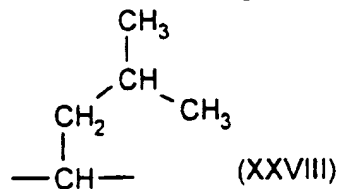
This invention also includes a polymer of one or  
 more alpha-olefins of the formula  $\text{CH}_2=\text{CH}(\text{CH}_2)_a\text{H}$  wherein  
 25  $a$  is an integer of 2 or more, wherein said polymer  
 contains methyl branches and said methyl branches  
 comprise about 25 to about 75 mole percent of the total  
 branches.

This invention also concerns a polyethylene  
 30 containing the structure (XXVII) in an amount greater  
 than can be accounted for by end groups, and preferably  
 at least 0.5 or more of such branches per 1000  
 methylene groups than can be accounted for by end  
 groups.

35

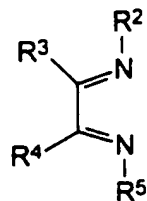


This invention also concerns a polypropylene containing one or both of the structures (XXVIII) and (XXIX) and in the case of (XXIX) in amounts greater than can be accounted for by end groups. Preferably at least 0.5 more of (XXIX) branches per 1000 methylene groups than can be accounted for by end groups, and/or at least 0.5 more of (XXVIII) per 1000 methylene groups are present in the polypropylene.

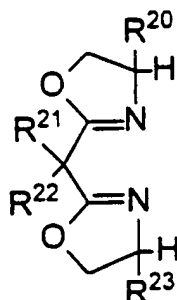
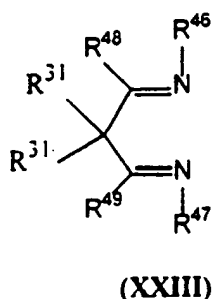
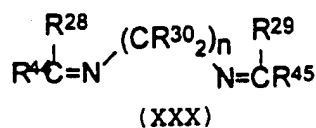


Also described herein is an ethylene homopolymer with a density of 0.86 g/ml or less.

Described herein is a process for the polymerization of olefins, comprising, contacting a transition metal complex of a bidentate ligand selected from the group consisting of



(VIII)



(XXXII)

5

with an olefin wherein:

said olefin is selected from the group consisting of ethylene, an olefin of the formula  $\text{R}^{17}\text{CH}=\text{CH}_2$  or  $\text{R}^{17}\text{CH}=\text{CHR}^{17}$ , cyclobutene, cyclopentene,

10 norbornene, or substituted norbornene;

said transition metal is selected from the group consisting of Ti, Zr, Sc, V, Cr, a rare earth metal, Fe, Co, Ni or Pd;

15  $\text{R}^2$  and  $\text{R}^5$  are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

$\text{R}^3$  and  $\text{R}^4$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or  $\text{R}^3$  and  $\text{R}^4$

taken together are hydrocarbylene substituted hydrocarbylene to form a carbocyclic ring;

$R^{44}$  is hydrocarbyl or substituted hydrocarbyl, and  $R^{28}$  is hydrogen, hydrocarbyl or substituted hydrocarbyl or  $R^{44}$  and  $R^{28}$  taken together form a ring;

$R^{45}$  is hydrocarbyl or substituted hydrocarbyl, and  $R^{29}$  is hydrogen, substituted hydrocarbyl or hydrocarbyl, or  $R^{45}$  and  $R^{29}$  taken together form a ring;

each  $R^{30}$  is independently hydrogen, substituted hydrocarbyl or hydrocarbyl, or two of  $R^{30}$  taken together form a ring;

$R^{20}$  and  $R^{23}$  are independently hydrocarbyl or substituted hydrocarbyl;

$R^{21}$  and  $R^{22}$  are each independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

each  $R^{17}$  is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

$n$  is 2 or 3;

$R^1$  is hydrogen, hydrocarbyl or substituted hydrocarbyl;

and provided that:

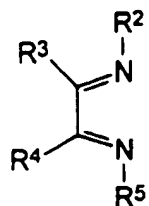
said transition metal also has bonded to it a ligand that may be displaced by said olefin or add to said olefin;

when  $M$  is Pd, said bidentate ligand is (VIII), (XXXII) or (XXIII);

when  $M$  is Pd a diene is not present; and

when norbornene or substituted norbornene is used no other olefin is present.

Described herein is a process for the copolymerization of an olefin and a fluorinated olefin, comprising, contacting a transition metal complex of a bidentate ligand selected from the group consisting of



(VIII)

with an olefin, and a fluorinated olefin wherein:

5        said olefin is selected from the group  
consisting of ethylene and an olefin of the formula  
 $R^{17}CH=CH_2$  or  $R^{17}CH=CHR^{17}$ ;

      said transition metal is selected from the  
group consisting of Ni and Pd;

10        said fluorinated olefin is of the formula  
 $H_2C=CH(CH_2)_aR_fR^{42}$ ;

      a is an integer of 2 to 20;  $R_f$  is  
perfluoroalkylene optionally containing one or more  
ether groups;

15         $R^{42}$  is fluorine or a functional group;

$R^2$  and  $R^5$  are each independently hydrocarbyl or  
substituted hydrocarbyl, provided that the carbon atom  
bound to the imino nitrogen atom has at least two  
carbon atoms bound to it;

20         $R^3$  and  $R^4$  are each independently hydrogen,  
hydrocarbyl, substituted hydrocarbyl, or  $R^3$  and  $R^4$   
taken together are hydrocarbylene substituted  
hydrocarbylene to form a carbocyclic ring;

      each  $R^{17}$  is independently saturated  
25 hydrocarbyl;

      and provided that said transition metal also has  
bonded to it a ligand that may be displaced by said  
olefin or add to said olefin.

      This invention also concerns a copolymer of an  
30 olefin of the formula  $R^{17}CH=CHR^{17}$  and a fluorinated  
olefin of the formula  $H_2C=CH(CH_2)_aR_fR^{42}$ , wherein:

      each  $R^{17}$  is independently hydrogen or saturated  
hydrocarbyl;

a is an integer of 2 to 20;  $R_f$  is perfluoroalkylene optionally containing one or more ether groups; and

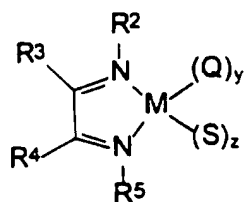
$R^{42}$  is fluorine or a functional group;

5 provided that when both of  $R^{17}$  are hydrogen and  $R^{42}$  is fluorine,  $R_f$  is  $-(CF_2)_b-$  wherein b is 2 to 20 or perfluoroalkylene containing at least one ether group.

Described herein is a process for the polymerization of olefins, comprising, contacting, at a  
10 temperature of about  $-100^\circ\text{C}$  to about  $+200^\circ\text{C}$ :

a first compound W, which is a neutral Lewis acid capable of abstracting either  $Q^-$  or  $S^-$  to form  $WQ^-$  or  $WS^-$ , provided that the anion formed is a weakly coordinating anion; or a cationic Lewis or Bronsted  
15 acid whose counterion is a weakly coordinating anion;

a second compound of the formula



(XI)

20

and one or more monomers selected from the group consisting of ethylene, an olefin of the formula  $R^{17}CH=CH_2$  or  $R^{17}CH=CHR^{17}$ , cyclobutene, cyclopentene, substituted norbornene, or norbornene;

25 wherein:

M is Ti, Zr, Sc, V, Cr, a rare earth metal, Fe, Co, Ni or Pd the m oxidation state;

$$y + z = m$$

30  $R^2$  and  $R^5$  are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

$R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or  $R^3$  and  $R^4$  taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

5        each  $R^{17}$  is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

10        Q is alkyl, hydride, chloride, iodide, or bromide;

         S is alkyl, hydride, chloride, iodide, or bromide; and

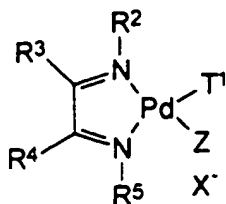
         provided that:

15        when norbornene or substituted norbornene is present, no other monomer is present;

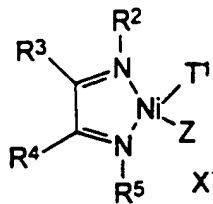
         when M is Pd a diene is not present; and

         except when M is Pd, when both Q and S are each independently chloride, bromide or iodide W is capable  
20        of transferring a hydride or alkyl group to M.

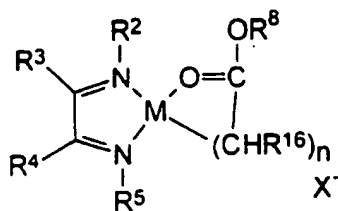
         This invention includes a process for the production of polyolefins, comprising contacting, at a temperature of about  $-100^{\circ}\text{C}$  to about  $+200^{\circ}\text{C}$ , one or more monomers selected from the group consisting of  
25        ethylene, an olefin of the formula  $R^{17}\text{CH}=\text{CH}_2$  or  $R^{17}\text{CH}=\text{CHR}^{17}$ , cyclobutene, cyclopentene, substituted norbornene, and norbornene; with a compound of the formula



(II)



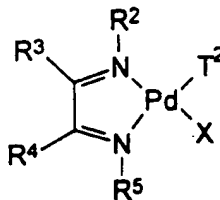
(III)



(IV)

5

or



(VII)

wherein:

10  $R^2$  and  $R^5$  are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

15  $R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or  $R^3$  and  $R^4$  taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

$T^1$  is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds,  $R^{15}C(=O)-$  or  $R^{15}OC(=O)-$ ;

20  $n$  is 2 or 3;

$Z$  is a neutral Lewis base wherein the donating atom is nitrogen, sulfur or oxygen, provided that if the donating atom is nitrogen then the  $pK_a$  of the conjugate acid of that compound is less than about 6;



X is a weakly coordinating anion;

$R^{15}$  is hydrocarbyl not containing olefinic or acetylenic bonds;

5 each  $R^{17}$  is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

M is Ni(II) or Pd(II);

10 each  $R^{16}$  is independently hydrogen or alkyl containing 1 to 10 carbon atoms;

n is 1, 2, or 3;

$R^6$  is hydrocarbyl; and

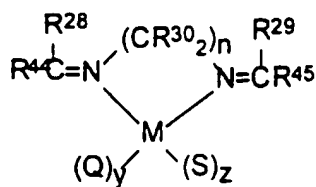
15  $T^2$  is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, hydrocarbyl substituted with keto or ester groups but not containing olefinic or acetylenic bonds,  $R^{15}C(=O)-$  or  $R^{15}OC(=O)-$ ;

and provided that:

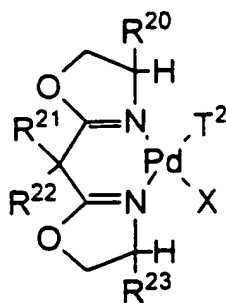
20 when M is Pd a diene is not present; and when norbornene or substituted norbornene is used no other monomer is present.

This invention includes a process for the production of polyolefins, comprising contacting, at a temperature of about  $-100^{\circ}C$  to about  $+200^{\circ}C$ , one or  
25 more monomers selected from the group consisting of ethylene, an olefin of the formula  $R^{17}CH=CH_2$  or  $R^{17}CH=CHR^{17}$ , cyclobutene, cyclopentene, substituted norbornene, and norbornene; with a compound of the formula

30

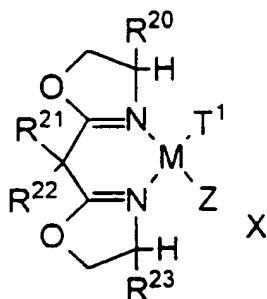


(XVII)



(XVIII)

or



(XIII)

wherein:

- 5  $R^{44}$  is hydrocarbyl or substituted hydrocarbyl,  
and  $R^{28}$  is hydrogen, hydrocarbyl or substituted  
hydrocarbyl or  $R^{44}$  and  $R^{28}$  taken together form a ring;  
 $R^{45}$  is hydrocarbyl or substituted hydrocarbyl,  
and  $R^{29}$  is hydrogen, substituted hydrocarbyl or  
10 hydrocarbyl, or  $R^{45}$  and  $R^{29}$  taken together form a ring;  
each  $R^{30}$  is independently hydrogen, substituted  
hydrocarbyl or hydrocarbyl, or two of  $R^{30}$  taken  
together form a ring;  
each  $R^{31}$  is independently hydrocarbyl or  
15 substituted hydrocarbyl provided that any olefinic bond  
in said olefin is separated from any other olefinic  
bond or aromatic ring by a quaternary carbon atom or at  
least two saturated carbon atoms;  
 $R^{20}$  and  $R^{23}$  are independently hydrocarbyl or  
20 substituted hydrocarbyl;  
 $R^{21}$  and  $R^{22}$  are each independently hydrogen,  
hydrocarbyl or substituted hydrocarbyl;

$T^1$  is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds,  $R^{15}C(=O)-$  or  $R^{15}CC(=O)-$ ;

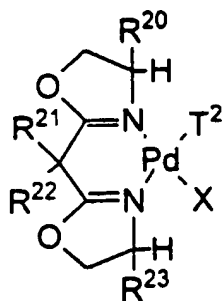
$Z$  is a neutral Lewis base wherein the donating atom is nitrogen, sulfur or oxygen, provided that if  
 5 the donating atom is nitrogen then the  $pK_a$  of the conjugate acid of that compound is less than about 6; and

$X$  is a weakly coordinating anion; and  
 provided that:

10 when  $M$  is Pd or (XVIII) is used a diene is not present; and

in (XVII)  $M$  is not Pd.

This invention includes a process for the production of polyolefins, comprising contacting, at a  
 15 temperature of about  $-100^\circ\text{C}$  to about  $+200^\circ\text{C}$ , one or more monomers selected from the group consisting of ethylene, an olefin of the formula  $R^{17}CH=CH_2$  or  $R^{17}CH=CHR^{17}$ , 4-vinylcyclohexene, cyclobutene, cyclopentene, substituted norbornene, and norbornene;  
 20 with a compound of the formula



(XVIII)

wherein:

25  $R^{20}$  and  $R^{23}$  are independently hydrocarbyl or substituted hydrocarbyl;

$R^{21}$  and  $R^{22}$  are each independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

$T^1$  is hydrogen, hydrocarbyl not containing  
 30 olefinic or acetylenic bonds,  $R^{15}C(=O)-$  or  $R^{15}OC(=O)-$ ;

Z is a neutral Lewis base wherein the donating atom is nitrogen, sulfur or oxygen, provided that if the donating atom is nitrogen then the pKa of the conjugate acid of that compound is less than about 6;

5 X is a weakly coordinating anion;

R<sup>15</sup> is hydrocarbyl not containing olefinic or acetylenic bonds;

each R<sup>17</sup> is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond  
10 in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

M is Ni(II) or Pd(II);

T<sup>2</sup> is hydrogen, hydrocarbyl not containing  
15 olefinic or acetylenic bonds, hydrocarbyl substituted with keto or ester groups but not containing olefinic or acetylenic bonds, R<sup>15</sup>C(=O)- or R<sup>15</sup>OC(=O)-;

and provided that:

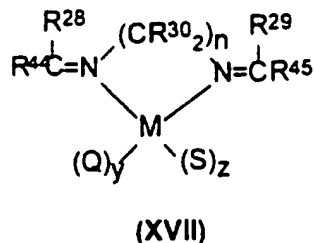
when M is Pd a diene is not present; and

20 when norbornene or substituted norbornene is used no other monomer is present.

Described herein is a process for the production for polyolefins, comprising contacting, at a temperature of about -100°C to about +200°C,

25 a first compound W, which is a neutral Lewis acid capable of abstracting either Q<sup>-</sup> or S<sup>-</sup> to form WQ<sup>-</sup> or WS<sup>-</sup>, provided that the anion formed is a weakly coordinating anion; or a cationic Lewis or Bronsted acid whose counterion is a weakly coordinating anion;

30 a second compound of the formula



and one or more monomers selected from the group consisting of ethylene, an olefin of the formula  $R^{17}CH=CH_2$  or  $R^{17}CH=CHR^{17}$ , cyclobutene, cyclopentene,

5 substituted norbornene, or norbornene;

wherein:

M is Ti, Zr, V, Cr, a rare earth metal, Co, Fe, Sc, or Ni, of oxidation state m;

$R^{44}$  is hydrocarbyl or substituted hydrocarbyl,

10 and  $R^{28}$  is hydrogen, substituted hydrocarbyl or hydrocarbyl, or  $R^{44}$  and  $R^{28}$  taken together form a ring;

$R^{45}$  is hydrocarbyl or substituted hydrocarbyl, and  $R^{29}$  is hydrogen, substituted hydrocarbyl or hydrocarbyl, or  $R^{45}$  and  $R^{29}$  taken together form a ring;

15 each  $R^{30}$  is independently hydrogen, substituted hydrocarbyl or hydrocarbyl, or two of  $R^{30}$  taken together form a ring;

n is 2 or 3;

y and z are positive integers;

20  $y+z = m$ ;

each  $R^{17}$  is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

25 Q is alkyl, hydride, chloride, iodide, or bromide;

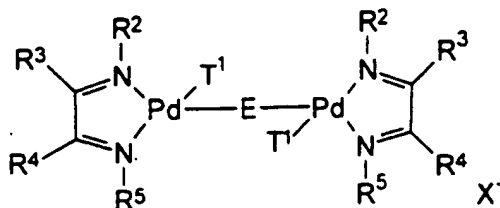
S is alkyl, hydride, chloride, iodide, or bromide; and

30 provided that;

when norbornene or substituted norbornene is present, no other monomer is present.

Disclosed herein is a process for the production of polyolefins, comprising, contacting, at a temperature of about  $-100^{\circ}C$  to about  $+200^{\circ}C$ , one or more monomers selected from the group consisting of ethylene, an olefin of the formula  $R^{17}CH=CH_2$  or  $R^{17}CH=CHR^{17}$ , cyclobutene, cyclopentene, substituted

norbornene, and norbornene; optionally a source of  $X^-$ ;  
with a compound of the formula



5

(V)

wherein:

$R^2$  and  $R^5$  are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it;

$R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or  $R^3$  and  $R^4$  taken together are hydrocarbylene substituted hydrocarbylene to form a ring;

each  $R^{17}$  is independently hydrocarbyl or substituted hydrocarbyl provided that  $R^{17}$  contains no olefinic bonds;

$T^1$  is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds,  $R^{15}C(=O)-$  or  $R^{15}OC(=O)-$ ;

$R^{15}$  is hydrocarbyl not containing olefinic or acetylenic bonds;

E is halogen or  $-OR^{18}$ ;

$R^{18}$  is hydrocarbyl not containing olefinic or acetylenic bonds; and

X is a weakly coordinating anion;

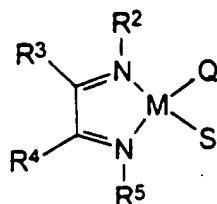
provided that, when norbornene or substituted norbornene is present, no other monomer is present.

Described herein is a process for the polymerization of olefins, comprising, contacting, at a temperature of about  $-100^\circ\text{C}$  to about  $+200^\circ\text{C}$ :

a first compound W, which is a neutral Lewis acid capable of abstracting either  $Q^-$  or  $S^-$  to form  $WQ^-$

or  $WS^-$ , provided that the anion formed is a weakly coordinating anion; or a cationic Lewis or Bronsted acid whose counterion is a weakly coordinating anion; a second compound of the formula

5



(I)

and one or more monomers selected from the group consisting of ethylene, an olefin of the formula  $R^{17}CH=CH_2$  or  $R^{17}CH=CHR^{17}$ , 4-vinylcyclohexene, cyclobutene, cyclopentene, substituted norbornene, or norbornene;

wherein:

15 M is Ni(II), Co(II), Fe(II), or Pd(II);

$R^2$  and  $R^5$  are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

20  $R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or  $R^3$  and  $R^4$  taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

25 each  $R^{17}$  is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

30 Q is alkyl, hydride, chloride, iodide, or bromide;

S is alkyl, hydride, chloride, iodide, or bromide; and

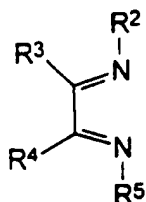
provided that;

when norbornene or substituted norbornene is present, no other monomer is present;

when M is Pd a diene is not present; and

except when M is Pd, when both Q and S are each independently chloride, bromide or iodide W is capable of transferring a hydride or alkyl group to M.

Included herein is a polymerization process, comprising, contacting a compound of the formula  $[Pd(R^{13}CN)_4]X_2$  or a combination of  $Pd[OC(O)R^{40}]_2$  and HX; a  
10 compound of the formula



(VIII)

15 and one or more monomers selected from the group consisting of ethylene, an olefin of the formula  $R^{17}CH=CH_2$  or  $R^{17}CH=CHR^{17}$ , cyclopentene, cyclobutene, substituted norbornene, and norbornene; wherein:

$R^2$  and  $R^5$  are each independently hydrocarbyl or  
20 substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

$R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or  $R^3$  and  $R^4$  taken  
25 together are hydrocarbylene or substituted hydrocarbylene to form a ring;

each  $R^{17}$  is independently hydrocarbyl or substituted hydrocarbyl provided that  $R^{17}$  contains no olefinic bonds;

30  $R^{13}$  is hydrocarbyl;

$R^{40}$  is hydrocarbyl or substituted hydrocarbyl

and

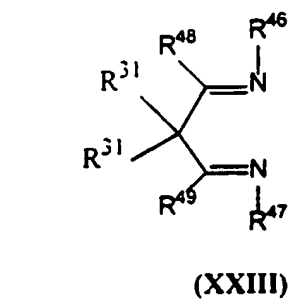
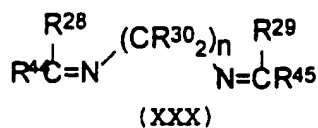
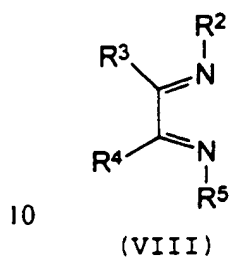
X is a weakly coordinating anion;



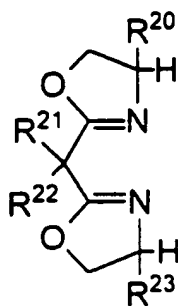
provided that, when norbornene or substituted norbornene is present, no other monomer is present.

Also described herein is a polymerization process, comprising;

- 5           contacting Ni[0], Pd[0] or Ni[I] compound containing a ligand which may be displaced by a ligand of the formula (VIII), (XXX), (XXXII) or (XXIII);
- a second compound of the formula



or



(XXXII)

an oxidizing agent;

a source of a relatively weakly coordinating anion;

- 5 and one or more monomers selected from the group consisting of ethylene, an olefin of the formula  $R^2-CH=CH_2$  or  $R^2-CH=CHR^{17}$ , cyclopentene, cyclobutene, substituted norbornene, and norbornene;

wherein:

- 10  $R^2$  and  $R^3$  are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

- $R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or  $R^3$  and  $R^4$  taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

- each  $R^2$  is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

$R^{13}$  is hydrocarbyl;

$R^{44}$  is hydrocarbyl or substituted hydrocarbyl,

- 25 and  $R^{28}$  is hydrogen, hydrocarbyl or substituted hydrocarbyl or  $R^{44}$  and  $R^{28}$  taken together form a ring;

$R^{45}$  is hydrocarbyl or substituted hydrocarbyl, and  $R^{29}$  is hydrogen, substituted hydrocarbyl or hydrocarbyl, or  $R^{45}$  and  $R^{29}$  taken together form a ring;

each  $R^{30}$  is independently hydrogen, substituted hydrocarbyl or hydrocarbyl, or two of  $R^{30}$  taken together form a ring;

5  $R^{46}$  and  $R^{47}$  are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

$R^{48}$  and  $R^{49}$  are each independently hydrogen, hydrocarbyl, or substituted hydrocarbyl;

10  $R^{20}$  and  $R^{23}$  are independently hydrocarbyl or substituted hydrocarbyl;

$n$  is 2 or 3;

$R^{21}$  and  $R^{22}$  are each independently hydrogen, hydrocarbyl or substituted hydrocarbyl; and

15  $X$  is a weakly coordinating anion;

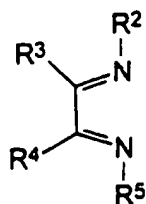
provided that;

when norbornene or substituted norbornene is present, no other monomer is present;

20 when said Pd[0] compound is used, a diene is not present; and

when said second compound is (XXX) only an Ni[0] or Ni[I] compound is used.

25 Described herein is a polymerization process, comprising, contacting an Ni[0] complex containing a ligand or ligands which may be displaced by (VIII), oxygen, an alkyl aluminum compound, and a compound of the formula



30 (VIII)

and one or more monomers selected from the group consisting of ethylene, an olefin of the formula

$R^{17}CH=CH_2$  or  $R^{17}CH=CHR^{17}$ , cyclopentene, cyclobutene, substituted norbornene, and norbornene; wherein:

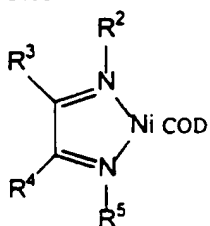
$R^2$  and  $R^5$  are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

$R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or  $R^3$  and  $R^4$  taken together are hydrocarbylene or substituted hydrocarbylene to form a ring; and

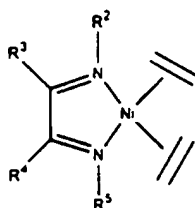
each  $R^{17}$  is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

provided that, when norbornene or substituted norbornene is present, no other monomer is present.

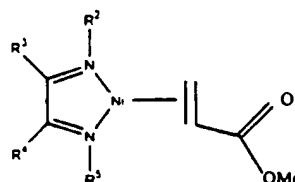
A polymerization process, comprising, contacting oxygen and an alkyl aluminum compound, or a compound of the formula HX, and a compound of the formula



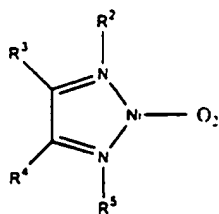
(XXXIII)



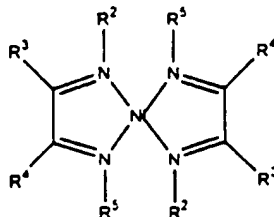
(XXXXII)



(XXXXIII)



(XXXXIV)



(XXXXV)

and one or more monomers selected from the group consisting of ethylene, an olefin of the formula

$R^{17}CH=CH_2$  or  $R^{17}CH=CHR^{17}$ , cyclopentene, cyclobutene, substituted norbornene, and norbornene; wherein:

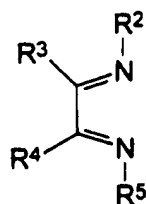
$R^2$  and  $R^5$  are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

5  $R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or  $R^3$  and  $R^4$  taken together are hydrocarbylene or substituted hydrocarbylene to form a ring; and

10 each  $R^{17}$  is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

15  $X$  is a weakly coordinating anion; and provided that, when norbornene or substituted norbornene is present, no other monomer is present.

Described herein is a polymerization process, comprising, contacting an  $Ni[0]$  complex containing a ligand or ligands which may be displaced by (VIII),  $HX$  or a Bronsted acidic solid, and a compound of the formula



(VIII)

25 and one or more monomers selected from the group consisting of ethylene, an olefin of the formula  $R^{17}CH=CH_2$ , or  $R^{17}CH=CHR^{17}$ , cyclopentene, cyclobutene, substituted norbornene, and norbornene; wherein:

30  $R^2$  and  $R^5$  are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

$R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or  $R^3$  and  $R^4$  taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

5 each  $R^{17}$  is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms; and

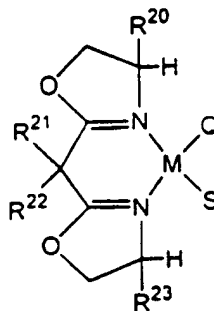
10 X is a weakly coordinating anion;

provided that, when norbornene or substituted norbornene is present, no other monomer is present

Described herein is a process for the polymerization of olefins, comprising, contacting, at a temperature of about  $-100^\circ\text{C}$  to about  $+200^\circ\text{C}$ :

15 a first compound W, which is a neutral Lewis acid capable of abstracting either  $Q^-$  or  $S^-$  to form  $WQ^-$  or  $WS^-$ , provided that the anion formed is a weakly coordinating anion; or a cationic Lewis or Bronsted acid whose counterion is a weakly coordinating anion;

20 a second compound of the formula



XIX

25 and one or more monomers selected from the group consisting of ethylene, an olefin of the formula  $R^{17}CH=CH_2$ , or  $R^{17}CH=CHR^{17}$ , cyclobutene, cyclopentene, substituted norbornene, or norbornene;

wherein:

30 M is Ni(II) or Pd(II);

$R^{20}$  and  $R^{23}$  are independently hydrocarbyl or substituted hydrocarbyl;

$R^{21}$  and  $R^{22}$  are each independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

5 each  $R^{17}$  is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

10 Q is alkyl, hydride, chloride, iodide, or bromide;

S is alkyl, hydride, chloride, iodide, or bromide; and

provided that;

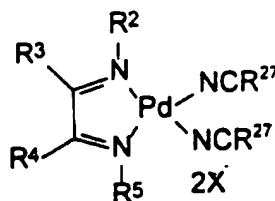
15 when norbornene or substituted norbornene is present, no other monomer is present;

when M is Pd a diene is not present; and

except when M is Pd, when both Q and S are each independently chloride, bromide or iodide W is capable  
20 of transferring a hydride or alkyl group to M.

This invention also concerns a process for the polymerization of olefins, comprising, contacting, at a temperature of about  $-100^{\circ}\text{C}$  to about  $+200^{\circ}\text{C}$ , a compound of the formula

25



(XIV)

30 and one or more monomers selected from the group consisting of ethylene, an olefin of the formula  $R^{17}\text{CH}=\text{CH}_2$  or  $R^{17}\text{CH}=\text{CHR}^{17}$ , cyclopentene, cyclobutene, substituted norbornene, and norbornene; wherein:

$R^2$  and  $R^5$  are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

5  $R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or  $R^3$  and  $R^4$  taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

10 each  $R^{17}$  is independently hydrocarbyl or substituted hydrocarbyl provided that  $R^{17}$  contains no olefinic bonds; and

each  $R^{27}$  is independently hydrocarbyl;

each X is a weakly coordinating anion;

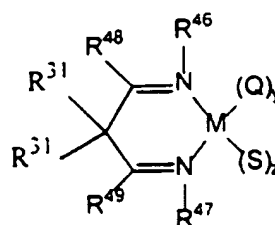
15 provided that, when norbornene or substituted norbornene is present, no other monomer is present.

This invention also concerns a process for the polymerization of olefins, comprising, contacting, at a temperature of about  $-100^\circ\text{C}$  to about  $+200^\circ\text{C}$ :

20 a first compound W, which is a neutral Lewis acid capable of abstracting either  $Q^-$  or  $S^-$  to form  $WQ^-$  or  $WS^-$ , provided that the anion formed is a weakly coordinating anion; or a cationic Lewis or Bronsted acid whose counterion is a weakly coordinating anion;

a second compound of the formula

25



(XV)

and one or more monomers selected from the group consisting of ethylene, an olefin of the formula  
30  $R^{17}CH=CH_2$  or  $R^{17}CH=CHR^{17}$ , cyclopentene, cyclobutene, substituted norbornene, and norbornene; wherein:



$R^{46}$  and  $R^{47}$  are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

5  $R^{48}$  and  $R^{49}$  are each independently hydrogen, hydrocarbyl, or substituted hydrocarbyl;

each  $R^{31}$  is independently hydrocarbyl, substituted hydrocarbyl or hydrogen;

10 M is Ti, Zr, Co, V, Cr, a rare earth metal, Fe, Sc, Ni, or Pd of oxidation state m;

y and z are positive integers;

$y+z = m$ ;

each  $R^{17}$  is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond  
15 in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

Q is alkyl, hydride, chloride, iodide, or bromide;

20 S is alkyl, hydride, chloride, iodide, or bromide; and

provided that;

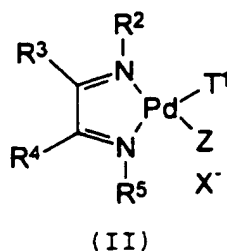
when norbornene or substituted norbornene is present, no other monomer is present;

25 when M is Pd a diene is not present; and

except when M is Pd, when both Q and S are each independently chloride, bromide or iodide W is capable of transferring a hydride or alkyl group to M.

Disclosed herein is a compound of the formula

30



wherein:

$R^2$  and  $R^5$  are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two  
5 carbon atoms bound to it;

$R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or  $R^3$  and  $R^4$  taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

10  $T^1$  is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds,  $R^{15}C(=O)-$  or  $R^{15}OC(=O)-$ ;

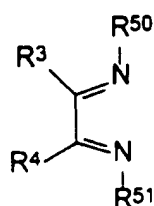
$Z$  is a neutral Lewis base wherein the donating atom is nitrogen, sulfur or oxygen, provided that if the donating atom is nitrogen then the  $pK_a$  of the  
15 conjugate acid of that compound is less than about 6;

$X$  is a weakly coordinating anion; and

$R^{15}$  is hydrocarbyl not containing olefinic or acetylenic bonds;

provided that when  $R^3$  and  $R^4$  taken together are  
20 hydrocarbylene to form a carbocyclic ring,  $Z$  is not an organic nitrile.

Described herein is a compound of the formula



wherein:

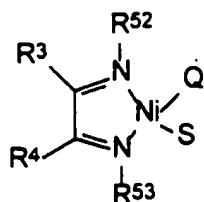
25  $R^{50}$  is substituted phenyl;

$R^{51}$  is phenyl or substituted phenyl;

$R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or  $R^3$  and  $R^4$  taken together are hydrocarbylene or substituted  
30 hydrocarbylene to form a ring;

and provided that groups in the 2 and 6 positions of  $R^{50}$  have a difference in  $E_s$  of about 0.60 or more.

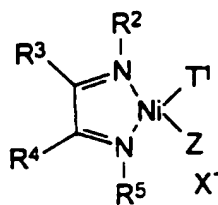
Described herein is a compound of the formula



(XXXVI)

wherein:

- 5        R<sup>52</sup> is substituted phenyl;  
        R<sup>53</sup> is phenyl or substituted phenyl;  
        R<sup>3</sup> and R<sup>4</sup> are each independently hydrogen,  
        hydrocarbyl, substituted hydrocarbyl or R<sup>3</sup> and R<sup>4</sup> taken  
        together are hydrocarbylene or substituted  
 10    hydrocarbylene to form a ring;  
        Q is alkyl, hydride, chloride, bromide or  
        iodide;  
        S is alkyl, hydride, chloride, bromide or  
        iodide;  
 15    and provided that;  
        groups in the 2 and 6 positions of R<sup>52</sup> have a  
        difference in E<sub>s</sub> of 0.15 or more; and  
        when both Q and S are each independently chloride,  
        bromide or iodide W is capable of transferring a  
 20    hydride or alkyl group to Ni.  
        This invention includes a compound of the formula



(III)

25

wherein:

- R<sup>2</sup> and R<sup>5</sup> are each independently hydrocarbyl or  
        substituted hydrocarbyl, provided that the carbon atom

bound to the imino nitrogen atom has at least two carbon atoms bound to it;

$R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, or substituted hydrocarbyl or  $R^3$  and  $R^4$  taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

$T^1$  is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds,  $R^{15}C(=O)-$  or  $R^{15}OC(=O)-$ ;

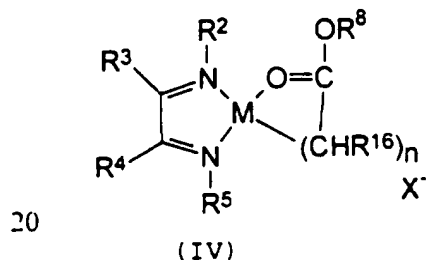
$R^{15}$  is hydrocarbyl not containing an olefinic or acetylenic bond;

$Z$  is a neutral Lewis acid wherein the donating atom is nitrogen, sulfur or oxygen, provided that, if the donating atom is nitrogen, then the  $pK_a$  of the conjugate acid of that compound is less than about 6;

and

$X$  is a weakly coordinating anion.

This invention also concerns a compound of the formula



wherein:

$R^2$  and  $R^5$  are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

$R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or  $R^3$  and  $R^4$  taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

$M$  is Ni(II) or Pd(II);

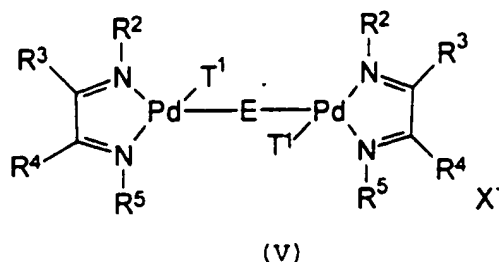
each  $R^{16}$  is independently hydrogen or alkyl  
containing 1 to 10 carbon atoms;

$n$  is 1, 2, or 3;

$X$  is a weakly coordinating anion; and

5  $R^8$  is hydrocarbyl.

Also disclosed herein is a compound of the formula



10

wherein:

$R^2$  and  $R^5$  are each independently hydrocarbyl or  
substituted hydrocarbyl, provided that the carbon atom  
bound directly to the imino nitrogen atom has at least  
15 two carbon atoms bound to it;

$R^3$  and  $R^4$  are each independently hydrogen,  
hydrocarbyl, substituted hydrocarbyl or  $R^3$  and  $R^4$  taken  
together are hydrocarbylene or substituted  
hydrocarbylene to form a ring;

20  $E$  is halogen or  $-OR^{18}$ ;

$R^{18}$  is hydrocarbyl not containing olefinic or  
acetylenic bonds;

$T^1$  is hydrogen, hydrocarbyl not containing  
olefinic or acetylenic bonds,  $R^{15}C(=O)-$  or  $R^{15}OC(=O)-$ ;

25  $R^{15}$  is hydrocarbyl not containing olefinic or  
acetylenic bonds; and

$X$  is a weakly coordinating anion.

Included herein is a compound of the formula  $[(\eta^4-1,5-COD)PdT^1Z]^+X^-$ , wherein:

30  $T^1$  is hydrocarbyl not containing olefinic or  
acetylenic bonds;

$X$  is a weakly coordinating anion;

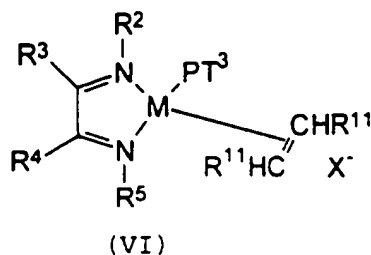
COD is 1,5-cyclooctadiene;

Z is  $R^{10}CN$ ; and

$R^{10}$  is hydrocarbyl not containing olefinic or acetylenic bonds.

Also included herein is a compound of the formula

5



wherein:

10

M is Ni(II) or Pd(II);

$R^2$  and  $R^5$  are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it;

15

$R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or  $R^3$  and  $R^4$  taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

20

each  $R^{11}$  is independently hydrogen, alkyl or  $-(CH_2)_mCO_2R^1$ ;

$T^3$  is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, or  $-CH_2CH_2CH_2CO_2R^8$ ;

25

P is a divalent group containing one or more repeat units derived from the polymerization of one or more of ethylene, an olefin of the formula  $R^{17}CH=CH_2$  or  $R^{17}CH=CHR^{17}$ , cyclobutene, cyclopentene, substituted norbornene, or norbornene and, when M is Pd(II), optionally one or more of: a compound of the formula  $CH_2=CH(CH_2)_mCO_2R^1$ , CO, or a vinyl ketone;

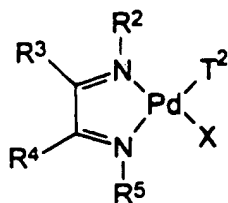
30

$R^8$  is hydrocarbyl;

m is 0 or an integer from 1 to 16;

$R^1$  is hydrogen, or hydrocarbyl or substituted hydrocarbyl containing 1 to 10 carbon atoms;

and X is a weakly coordinating anion;  
 provided that, when M is Ni(II),  $R^{11}$  is not  $-\text{CO}_2\text{R}^8$ .  
 Also described herein is a compound of the formula



5

(VII)

wherein:

$R^2$  and  $R^5$  are each independently hydrocarbyl or  
 10 substituted hydrocarbyl, provided that the carbon atom  
 bound to the imino nitrogen atom has at least two  
 carbon atoms bound to it;

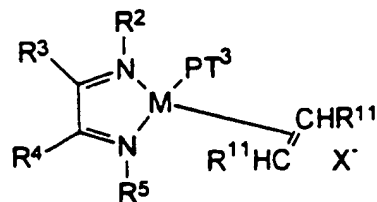
$R^3$  and  $R^4$  are each independently hydrogen,  
 hydrocarbyl, substituted hydrocarbyl or  $R^3$  and  $R^4$  taken  
 15 together are hydrocarbylene or substituted  
 hydrocarbylene to form a ring;

$T^2$  is hydrogen, hydrocarbyl not containing  
 olefinic or acetylenic bonds, hydrocarbyl substituted  
 with keto or ester groups but not containing olefinic  
 20 or acetylenic bonds,  $R^{15}\text{C}(=\text{O})-$  or  $\text{R}^{15}\text{OC}(=\text{O})-$ ;

$R^{15}$  is hydrocarbyl not containing olefinic or  
 acetylenic bonds; and

X is a weakly coordinating anion.

Included herein is a process for the production of  
 25 polyolefins, comprising, contacting, at a temperature  
 of about  $-100^\circ\text{C}$  to about  $+200^\circ\text{C}$ , a compound of the  
 formula



(VI)

and one or more monomers selected from the group consisting of ethylene, an olefin of the formula  $R^{17}CH=CH_2$  or  $R^{17}CH=CHR^{17}$ , cyclobutene, cyclopentene,  
5 substituted norbornene, and norbornene,

wherein:

M is Ni(II) or Pd(II);

$R^2$  and  $R^5$  are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom  
10 bound directly to the imino nitrogen atom has at least two carbon atoms bound to it;

$R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or  $R^3$  and  $R^4$  taken together are hydrocarbylene or substituted  
15 hydrocarbylene to form a ring;

each  $R^{11}$  is independently hydrogen, alkyl or  $-(CH_2)_mCO_2R^1$ ;

$T^3$  is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, or  $-CH_2CH_2CH_2CO_2R^8$ ;

20 P is a divalent group containing one or more repeat units derived from the polymerization of one or monomers selected from the group consisting of ethylene, an olefin of the formula  $R^{17}CH=CH_2$  or  $R^{17}CH=CHR^{17}$ , cyclopentene, cyclobutene, substituted  
25 norbornene, and norbornene, and, when M is Pd(II), optionally one or more of: a compound of the formula  $CH_2=CH(CH_2)_mCO_2R^1$ , CO or a vinyl ketone;

$R^8$  is hydrocarbyl;

each  $R^{17}$  is independently hydrocarbyl or  
30 substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;  $R^1$  is hydrogen, or hydrocarbyl or substituted hydrocarbyl containing 1 to  
35 10 carbon atoms;

m is 0 or an integer of 1 to 16;

and X is a weakly coordinating anion;



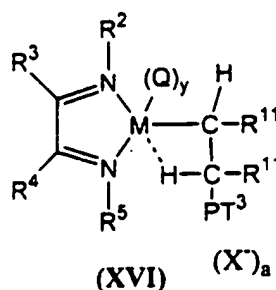
provided that:

when M is Pd a diene is not present;

when norbornene or substituted norbornene is present, no other monomer is present; and

5 further provided that, when M is Ni(II),  $R^{11}$  is not  $-\text{CO}_2\text{R}^8$ .

Included herein is a process for the production of polyolefins, comprising, contacting, at a temperature  
10 of about  $-100^\circ\text{C}$  to about  $+200^\circ\text{C}$ , a compound of the formula



15 and one or more monomers selected from the group consisting of ethylene, an olefin of the formula  $\text{R}^{17}\text{CH}=\text{CH}_2$ , or  $\text{R}^{17}\text{CH}=\text{CHR}^{17}$ , cyclobutene, cyclopentene, substituted norbornene, and norbornene,

wherein:

20 M is Zr, Ti, Sc, V, Cr, a rare earth metal, Fe, Co, Ni or Pd of oxidation state m;

$R^2$  and  $R^5$  are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least  
25 two carbon atoms bound to it;

$R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or  $R^3$  and  $R^4$  taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

30 each  $R^{11}$  is independently hydrogen, or alkyl, or both of  $R^{11}$  taken together are hydrocarbylene to form a carbocyclic ring;

$T^1$  is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, or  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{R}^8$ ;

P is a divalent group containing one or more repeat units derived from the polymerization of one or  
 5 monomers selected from the group consisting of ethylene, an olefin of the formula  $\text{R}^{17}\text{CH}=\text{CH}_2$  or  $\text{R}^{17}\text{CH}=\text{CHR}^{17}$ , cyclopentene, cyclobutene, substituted norbornene, and norbornene, and, when M is Pd(II), optionally one or more of: a compound of the formula  
 10  $\text{CH}_2=\text{CH}(\text{CH}_2)_m\text{CO}_2\text{R}^1$ , CO, or a vinyl ketone;

$\text{R}^8$  is hydrocarbyl;

a is 1 or 2;

$y + a + 1 = m$ ;

each  $\text{R}^{17}$  is independently hydrocarbyl or  
 15 substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;  $\text{R}^2$  is hydrogen, or hydrocarbyl or substituted hydrocarbyl containing 1 to  
 20 10 carbon atoms;

m is 0 or an integer of 1 to 16;

and X is a weakly coordinating anion;

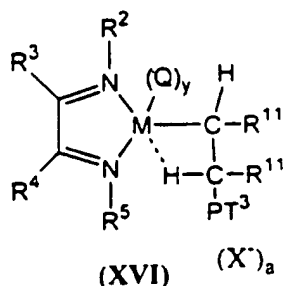
provided that:

when norbornene or substituted norbornene is  
 25 present, no other monomer is present;

when M is Pd a diene is not present; and

further provided that, when M is Ni(II),  $\text{R}^{11}$  is not  
 $-\text{CO}_2\text{R}^8$ .

30 Also described herein is a compound of the formula



wherein:

M is Zr, Ti, Sc, V, Cr, a rare earth metal, Fe, Co, Ni or Pd of oxidation state m;

5         $R^2$  and  $R^5$  are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it;

10         $R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or  $R^3$  and  $R^4$  taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

15        each  $R^{11}$  is independently hydrogen, or alkyl, or both of  $R^{11}$  taken together are hydrocarbylene to form a carbocyclic ring;

$T^3$  is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, or  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{R}^8$ ;

20        P is a divalent group containing one or more repeat units derived from the polymerization of one or monomers selected from the group consisting of ethylene, an olefin of the formula  $\text{R}^{17}\text{CH}=\text{CH}_2$  or  $\text{R}^{17}\text{CH}=\text{CHR}^{17}$ , cyclopentene, cyclobutene, substituted norbornene, and norbornene, and optionally, when M is Pd(II), one or more of: a compound of the formula  
25         $\text{CH}_2=\text{CH}(\text{CH}_2)_m\text{CO}_2\text{R}^1$ , CO, or a vinyl ketone;

Q is a monovalent anion;

$\text{R}^8$  is hydrocarbyl;

a is 1 or 2;

$y + a + 1 = m$ ;

30        each  $\text{R}^{17}$  is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

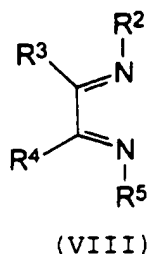
35         $\text{R}^1$  is hydrogen, or hydrocarbyl or substituted hydrocarbyl containing 1 to 10 carbon atoms;

m is 0 or an integer of 1 to 16; and

and X is a weakly coordinating anion;

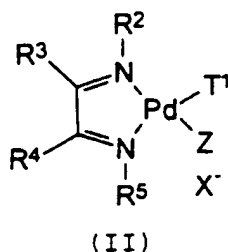
and provided that when M is Pd a diene is not present.

Described herein is a process, comprising, contacting, at a temperature of about  $-40^{\circ}\text{C}$  to about  
 5  $+60^{\circ}\text{C}$ , a compound of the formula  $[(\eta^4\text{-}1,5\text{-COD})\text{Pd}^{\text{T}^1}\text{Z}]\text{X}^-$  and a diimine of the formula



10

to produce a compound of the formula



15

wherein:

$\text{T}^1$  is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds,  $\text{R}^{15}\text{C}(=\text{O})-$  or  $\text{R}^{15}\text{OC}(=\text{O})-$ ;

X is a weakly coordinating anion;

20

COD is 1,5-cyclooctadiene;

Z is  $\text{R}^{10}\text{CN}$ ;

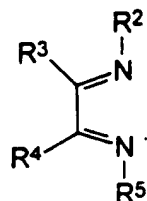
$\text{R}^{10}$  is hydrocarbyl not containing olefinic or acetylenic bonds;

25  $\text{R}^{15}$  is hydrocarbyl not containing olefinic or acetylenic bonds;

$\text{R}^2$  and  $\text{R}^5$  are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and

$R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or  $R^3$  and  $R^4$  taken together are hydrocarbylene or substituted hydrocarbylene to form a ring.

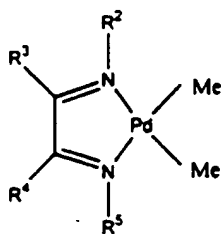
- 5 Described herein is a process, comprising, contacting, at a temperature of about  $-80^{\circ}\text{C}$  to about  $+20^{\circ}\text{C}$ , a compound of the formula  $(\eta^4\text{-}1,5\text{-COD})\text{PdMe}_2$  and a diimine of the formula



10

(VIII)

to produce a compound of the formula



15

(XXXXI)

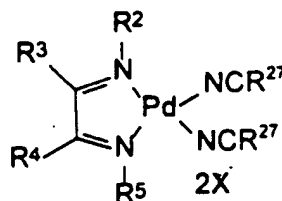
wherein:

COD is 1,5-cyclooctadiene;

- 20  $R^2$  and  $R^5$  are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and

- 25  $R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or  $R^3$  and  $R^4$  taken together are hydrocarbylene or substituted hydrocarbylene to form a ring.

Also disclosed herein is a compound of the formula



(XIV)

5

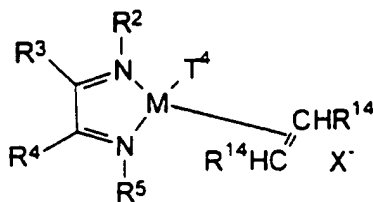
wherein:

- $R^2$  and  $R^5$  are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

- $R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or  $R^3$  and  $R^4$  taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

- each  $R^{27}$  is hydrocarbyl; and  
each X is a weakly coordinating anion.

This invention includes a compound of the formula



20

(IX)

wherein:

M is Ni(II) or Pd(II);

- $R^2$  and  $R^5$  are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it;

$R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or  $R^3$  and  $R^4$  taken

together are hydrocarbylene or substituted hydrocarbylene to form a ring;

each  $R^{14}$  is independently hydrogen, alkyl or  $-(CH_2)_mCO_2R^1$ ;

5  $R^1$  is hydrogen, or hydrocarbyl or substituted hydrocarbyl containing 1 to 10 carbon atoms;

$T^4$  is alkyl,  $-R^{60}C(O)OR^8$ ,  $R^{15}(C=O)-$  or  $R^{15}OC(=O)-$

10  $R^{15}$  is hydrocarbyl not containing olefinic or acetylenic bonds;

$R^{60}$  is alkylene not containing olefinic or acetylenic bonds;

$R^8$  is hydrocarbyl;;

and X is a weakly coordinating anion;

15 and provided that when  $R^{14}$  is  $-(CH_2)_mCO_2R^1$ , or  $T^4$  is not alkyl, M is Pd(II).

Described herein is a homopolypropylene with a glass transition temperature of  $-30^\circ C$  or less, and containing at least about 50 branches per 1000 methylene groups.

20 This invention also concerns a homopolymer of cyclopentene having a degree of polymerization of about 30 or more and an end of melting point of about  $100^\circ C$  to about  $320^\circ C$ , provided that said homopolymer has less than 5 mole percent of enchaind linear olefin containing pentylene units.

In addition, disclosed herein is a homopolymer or copolymer of cyclopentene that has an X-ray powder diffraction pattern that has reflections at approximately  $17.3^\circ$ ,  $19.3^\circ$ ,  $24.2^\circ$ , and  $40.7^\circ$   $2\theta$ .

30 Another novel polymer is a homopolymer of cyclopentene wherein at least 90 mole percent of enchaind cyclopentylene units are 1,3-cyclopentylene units, and said homopolymer has an average degree of polymerization of 30 more.

35 Described herein is a homopolymer of cyclopentene wherein at least 90 mole percent of enchaind cyclopentylene units are cis-1,3-cyclopentylene, and

said homopolymer has an average degree of polymerization of about 10 or more.

Also described is a copolymer of cyclopentene and ethylene wherein at least 75 mole percent of enchain-  
5 cyclopentylene units are 1,3-cyclopentylene units.

This invention concerns a copolymer of cyclopentene and ethylene wherein there are at least 20 branches per 1000 methylene carbon atoms.

Described herein is a copolymer of cyclopentene  
10 and ethylene wherein at least 50 mole percent of the repeat units are derived from cyclopentene.

Disclosed herein is a copolymer of cyclopentene and an  $\alpha$ -olefin.

This invention also concerns a polymerization  
15 process, comprising, contacting an olefin of the formula  $R^{17}CH=CH_2$  or  $R^{17}CH=CHR^{17}$ , wherein each  $R^{17}$  is independently hydrogen, hydrocarbyl, or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or  
20 aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms with a catalyst, wherein said catalyst:

contains a nickel or palladium atom in a positive oxidation state;

25 contains a neutral bidentate ligand coordinated to said nickel or palladium atom, and wherein coordination to said nickel or palladium atom is through two nitrogen atoms or a nitrogen atom and a phosphorous atom; and

30 said neutral bidentate ligand, has an Ethylene Exchange Rate of less than  $20,000 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$  when said catalyst contains a palladium atom, and less than  $50,000 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$  when said catalyst contains a nickel atom;

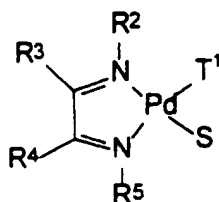
35 and provided that when Pd is present a diene is not present.



Described herein is a process for the polymerization of olefins, comprising, contacting, at a temperature of about  $-100^{\circ}\text{C}$  to about  $+200^{\circ}\text{C}$ :

- 5 a first compound which is a salt of an alkali metal cation and a relatively noncoordinating monoanion;

a second compound of the formula



10 (XX)

- and one or more monomers selected from the group consisting of ethylene, an olefin of the formula  $\text{R}^{17}\text{CH}=\text{CH}_2$  or  $\text{R}^{17}\text{CH}=\text{CHR}^{17}$ , cyclobutene, cyclopentene, substituted norbornene, or norbornene;
- 15

wherein:

- $\text{R}^2$  and  $\text{R}^5$  are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;
- 20

$\text{R}^3$  and  $\text{R}^4$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or  $\text{R}^3$  and  $\text{R}^4$  taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

- 25 each  $\text{R}^{17}$  is independently hydrocarbyl or substituted hydrocarbyl provided that  $\text{R}^{17}$  contains no olefinic bond;

$\text{T}^1$  is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds,  $\text{R}^{15}\text{C}(=\text{O})-$  or  $\text{R}^{15}\text{OC}(=\text{O})-$ ;

- 30 S is chloride, iodide, or bromide; and provided that, when norbornene or substituted norbornene is present, no other monomer is present.

Described herein is a polyolefin, comprising, a polymer made by polymerizing one or more monomers of the formula  $H_2C=CH(CH_2)_eG$  by contacting said monomers with a transition metal containing coordination

5 polymerization catalyst, wherein:

each G is independently hydrogen or  $-CO_2R^1$ ;

each e is independently 0 or an integer of 1 to 20;

each  $R^1$  is independently hydrogen, hydrocarbyl  
10 or substituted hydrocarbyl;

and provided that:

said polymer has at least 50 branches per 1000 methylene groups;

in at least 50 mole percent of said monomers G  
15 is hydrogen; and

except when no branches should be theoretically present, the number of branches per 1000 methylene groups is 90% or less than the number of theoretical branches per 1000 methylene groups, or the number of  
20 branches per 1000 methylene groups is 110% or more of theoretical branches per 1000 methylene groups, and

when there should be no branches theoretically present, said polyolefin has 50 or more branches per 1000 methylene groups;

25 and provided that said polyolefin has at least two branches of different lengths containing less than 6 carbon atoms each.

Also described herein is a polyolefin, comprising, a polymer made by polymerizing one or more monomers of  
30 the formula  $H_2C=CH(CH_2)_eG$  by contacting said monomers with a transition metal containing coordination polymerization catalyst, wherein:

each G is independently hydrogen or  $-CO_2R^1$ ;

each e is independently 0 or an integer of 1 to  
35 20;

$R^1$  is independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

and provided that:

said polymer has at least 50 branches per 1000 methylene groups;

in at least 50 mole percent of said monomers G is hydrogen;

- 5        said polymer has at least 50 branches of the formula  $-(CH_2)_eG$  per 1000 methylene groups, wherein when G is the same as in a monomer and  $e \neq f$ , and/or for any single monomer of the formula  $H_2C=CH(CH_2)_eG$  there are less than 90% of the number of theoretical branches per 1000 methylene groups, or more than 110% of the theoretical branches per 1000 methylene groups of the formula  $-(CH_2)_fG$  and  $f=e$ , and wherein f is 0 or an integer of 1 or more;

- 10       and provided that said polyolefin has at least two branches of different lengths containing less than 6 carbon atoms.

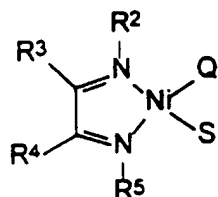
This invention concerns a process for the formation of linear  $\alpha$ -olefins, comprising, contacting, at a temperature of about  $-100^\circ\text{C}$  to about  $+200^\circ\text{C}$ :

- 20       ethylene;

a first compound W, which is a neutral Lewis acid capable of abstracting  $X^-$  to form  $WX^+$ , provided that the anion formed is a weakly coordinating anion, or a cationic Lewis or Bronsted acid whose counterion is a

- 25       weakly coordinating anion; and

a second compound of the formula



(XXXI)

wherein:

- 30        $R^2$  and  $R^5$  are each independently hydrocarbyl or substituted hydrocarbyl;

$R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or  $R^3$  and  $R^4$  taken

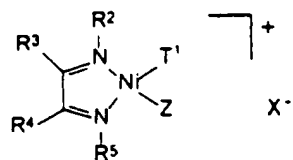
together are hydrocarbylene or substituted hydrocarbylene to form a ring; and

Q and S are each independently chlorine, bromine, iodine or alkyl; and

5 wherein an  $\alpha$ -olefin containing 4 to 40 carbon atoms is produced.

This invention also concerns a process for the formation of linear  $\alpha$ -olefins, comprising, contacting, at a temperature of about  $-100^{\circ}\text{C}$  to about  $+200^{\circ}\text{C}$ :

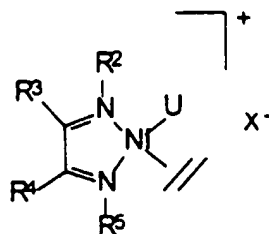
10 ethylene and a compound of the formula



(III)

or

15



(XXXIV)

wherein:

20 R<sup>2</sup> and R<sup>5</sup> are each independently hydrocarbyl or substituted hydrocarbyl;

R<sup>3</sup> and R<sup>4</sup> are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R<sup>3</sup> and R<sup>4</sup> taken together are hydrocarbylene or substituted

25 hydrocarbylene to form a ring;

T<sup>1</sup> is hydrogen or n-alkyl containing up to 38 carbon atoms;

Z is a neutral Lewis base wherein the donating atom is nitrogen, sulfur, or oxygen, provided that if

the donating atom is nitrogen then the pKa of the conjugate acid of that compound (measured in water) is less than about 6;

U is n-alkyl containing up to 38 carbon atoms;

5 and

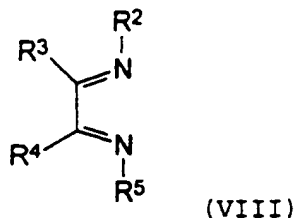
X is a noncoordinating anion;

and wherein an  $\alpha$ -olefin containing 4 to 40 carbon atoms is produced.

Another novel process is a process for the  
10 formation of linear  $\alpha$ -olefins, comprising, contacting,  
at a temperature of about  $-100^{\circ}\text{C}$  to about  $+200^{\circ}\text{C}$ :

ethylene;

and a Ni(II) of



15

$\text{R}^2$  and  $\text{R}^5$  are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

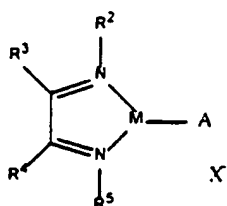
20

$\text{R}^3$  and  $\text{R}^4$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or  $\text{R}^3$  and  $\text{R}^4$  taken together are hydrocarbylene substituted hydrocarbylene to form a carbocyclic ring and

wherein an  $\alpha$ -olefin containing 4 to 40 carbon  
25 atoms is produced.

Also described herein is a process for the production of polyolefins, comprising, contacting, at a temperature of about  $0^{\circ}\text{C}$  to about  $+200^{\circ}\text{C}$ , a compound of the formula

30



XXXVII

and one or more monomers selected from the group consisting of ethylene, an olefin of the formula  
 5  $R^{17}CH=CH_2$  or  $R^{17}CH=CHR^{17}$ , cyclobutene, cyclopentene, substituted norbornene, and norbornene,

wherein:

M is Ni(II) or Pd(II);

A is a  $\pi$ -allyl or  $\pi$ -benzyl group;

10  $R^2$  and  $R^5$  are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it;

15  $R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or  $R^3$  and  $R^4$  taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

20 each  $R^{17}$  is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

and X is a weakly coordinating anion;

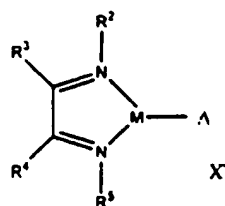
and provided that:

25 when M is Pd a diene is not present; and

when norbornene or substituted norbornene is present, no other monomer is present.

The invention also includes a compound of the formula

30



## XXXVII

wherein:

M is Ni(II) or Pd(II);

A is a  $\pi$ -allyl or  $\pi$ -benzyl group;

5  $R^2$  and  $R^5$  are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it;

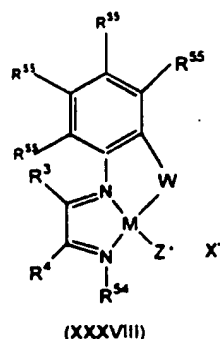
$R^3$  and  $R^4$  are each independently hydrogen,  
10 hydrocarbyl, substituted hydrocarbyl or  $R^3$  and  $R^4$  taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

each  $R^{17}$  is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond  
15 in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

and X is a weakly coordinating anion;

and provided that when M is Pd a diene is not  
20 present.

This invention also includes a compound of the formula



25

wherein:

$R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or  $R^3$  and  $R^4$  taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

$R^{54}$  is hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it;

each  $R^{55}$  is independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or a functional group;

W is alkylene or substituted alkylene containing 2 or more carbon atoms;

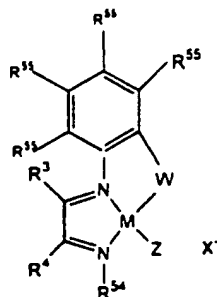
Z is a neutral Lewis base wherein the donating atom is nitrogen, sulfur, or oxygen, provided that if the donating atom is nitrogen then the pKa of the conjugate acid of that compound (measured in water) is less than about 6, or an olefin of the formula  $R^{17}CH=CHR^{17}$ ;

each  $R^{17}$  is independently hydrogen, saturated hydrocarbyl or substituted saturated hydrocarbyl; and

X is a weakly coordinating anion;

and provided that when M is Ni, W is alkylene and each  $R^{17}$  is independently hydrogen or saturated hydrocarbyl.

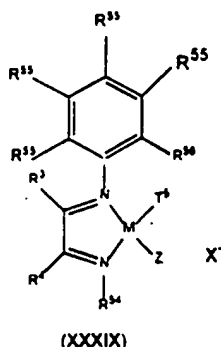
This invention also includes a process for the production of a compound of the formula



(XXXVIII)



comprising, heating a compound of the formula



at a temperature of about  $-30^{\circ}\text{C}$  to about  $+100^{\circ}$  for a  
 5 sufficient time to produce (XXXVIII), and wherein:

$\text{R}^3$  and  $\text{R}^4$  are each independently hydrogen,  
 hydrocarbyl, substituted hydrocarbyl or  $\text{R}^3$  and  $\text{R}^4$  taken  
 together are hydrocarbylene or substituted  
 hydrocarbylene to form a ring;

10  $\text{R}^{54}$  is hydrocarbyl or substituted hydrocarbyl,  
 provided that the carbon atom bound directly to the  
 imino nitrogen atom has at least two carbon atoms bound  
 to it;

each  $\text{R}^{55}$  is independently hydrogen,  
 15 hydrocarbyl, substituted hydrocarbyl, or a functional  
 group;

$\text{R}^{56}$  is alkyl containing 2 to 30 carbon atoms;

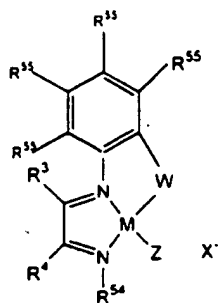
$\text{T}^5$  is alkyl;

W is alkylene containing 2 to 30 carbon atoms;

20 Z is a neutral Lewis base wherein the donating  
 atom is nitrogen, sulfur, or oxygen, provided that if  
 the donating atom is nitrogen then the pKa of the  
 conjugate acid of that compound (measured in water) is  
 less than about 6; and

25 X is a weakly coordinating anion.

This invention also concerns a process for the  
 polymerization of olefins, comprising, contacting a  
 compound of the formula



(XXXVIII)

and one or more monomers selected from the group consisting of ethylene, an olefin of the formula  $R^{17}CH=CH_2$  or  $R^{17}CH=CHR^{17}$ , cyclobutene, cyclopentene, substituted norbornene, and norbornene,

wherein:

$R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or  $R^3$  and  $R^4$  taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

$R^{54}$  is hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it;

each  $R^{55}$  is independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or a functional group;

W is alkylene or substituted alkylene containing 2 or more carbon atoms;

Z is a neutral Lewis base wherein the donating atom is nitrogen, sulfur, or oxygen, provided that if the donating atom is nitrogen then the pKa of the conjugate acid of that compound (measured in water) is less than about 6, or an olefin of the formula  $R^{17}CH=CHR^{17}$ ;

each  $R^{17}$  is independently hydrogen, saturated hydrocarbyl or substituted saturated hydrocarbyl; and

X is a weakly coordinating anion;

and provided that:

when M is Ni, W is alkylene and each  $R^{17}$  is independently hydrogen or saturated hydrocarbyl;

and when norbornene or substituted norbornene is present, no other monomer is present.

This invention also concerns a homopolypropylene containing about 10 to about 700  $\delta^+$  methylene groups per 1000 total methylene groups in said homopolypropylene.

Described herein is a homopolypropylene wherein the ratio of  $\delta^+:\gamma$  methylene groups is about 0.5 to about 7.

Also included herein is a homopolypropylene in which about 30 to about 85 mole percent of the monomer units are enchaind in an  $\omega,1$  fashion.

#### DETAILS OF THE INVENTION

Herein certain terms are used to define certain chemical groups or compounds. These terms are defined below.

- A "hydrocarbyl group" is a univalent group containing only carbon and hydrogen. If not otherwise stated, it is preferred that hydrocarbyl groups herein contain 1 to about 30 carbon atoms.

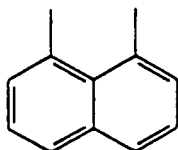
- By "not containing olefinic or acetylenic bonds" is meant the grouping does not contain olefinic carbon-carbon double bonds (but aromatic rings are not excluded) and carbon-carbon triple bonds.

- By "substituted hydrocarbyl" herein is meant a hydrocarbyl group which contains one or more substituent groups which are inert under the process conditions to which the compound containing these groups is subjected. The substituent groups also do not substantially interfere with the process. If not otherwise stated, it is preferred that substituted hydrocarbyl groups herein contain 1 to about 30 carbon atoms. Included in the meaning of "substituted" are heteroaromatic rings.

- By an alkyl aluminum compound is meant a compound in which at least one alkyl group is bound to an aluminum atom. Other groups such as alkoxide,

oxygen, and halogen may also be bound to aluminum atoms in the compound.

- By "hydrocarbylene" herein is meant a divalent group containing only carbon and hydrogen.
- 5 Typical hydrocarbylene groups are  $-(CH_2)_4-$ ,  $-CH_2CH(CH_2CH_3)CH_2CH_2-$  and



(An)

10

If not otherwise stated, it is preferred that hydrocarbylene groups herein contain 1 to about 30 carbon atoms.

- By "substituted hydrocarbylene" herein is meant a hydrocarbylene group which contains one or more substituent groups which are inert under the process conditions to which the compound containing these groups is subjected. The substituent groups also do not substantially interfere with the process. If not
- 15
- 20 otherwise stated, it is preferred that substituted hydrocarbylene groups herein contain 1 to about 30 carbon atoms. Included within the meaning of "substituted" are heteroaromatic rings.

- By substituted norbornene is meant a
- 25 norbornene which is substituted with one or more groups which does not interfere substantially with the polymerization. It is preferred that substituent groups (if they contain carbon atoms) contain 1 to 30 carbon atoms. Examples of substituted norbornenes are
- 30 ethylidene norbornene and methylene norbornene.

- By "saturated hydrocarbonyl" is meant a univalent group containing only carbon and hydrogen which contains no unsaturation, such as olefinic, acetylenic, or aromatic groups. Examples of such
- 35 groups include alkyl and cycloalkyl. If not otherwise

stated, it is preferred that saturated hydrocarbonyl groups herein contain 1 to about 30 carbon atoms.

- By "neutral Lewis base" is meant a compound, which is not an ion, which can act as a Lewis base.

5 Examples of such compounds include ethers, amines, sulfides, and organic nitriles.

- By "cationic Lewis acid" is meant a cation which can act as a Lewis acid. Examples of such cations are sodium and silver cations.

10 • By " $\alpha$ -olefin" is meant a compound of the formula  $\text{CH}_2=\text{CHR}^{19}$ , wherein  $\text{R}^{19}$  is n-alkyl or branched alkyl, preferably n-alkyl.

- By "linear  $\alpha$ -olefin" is meant a compound of the formula  $\text{CH}_2=\text{CHR}^{19}$ , wherein  $\text{R}^{19}$  is n-alkyl. It is preferred that the linear  $\alpha$ -olefin have 4 to 40 carbon atoms.

20 • By a "saturated carbon atom" is meant a carbon atom which is bonded to other atoms by single bonds only. Not included in saturated carbon atoms are carbon atoms which are part of aromatic rings.

- By a quaternary carbon atom is meant a saturated carbon atom which is not bound to any hydrogen atoms. A preferred quaternary carbon atom is bound to four other carbon atoms.

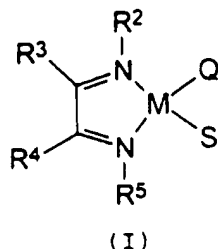
25 • By an olefinic bond is meant a carbon-carbon double bond, but does not include bonds in aromatic rings.

- By a rare earth metal is meant one of lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium or lutetium.

35 This invention concerns processes for making polymers, comprising, contacting one or more selected olefins or cycloolefins, and optionally an ester or carboxylic acid of the formula  $\text{CH}_2=\text{CH}(\text{CH}_2)_n\text{CO}_2\text{R}^2$ , and other selected monomers, with a transition metal containing catalyst (and possibly other catalyst

components). Such catalysts are, for instance, various complexes of a diimine with these metals. By a "polymerization process herein (and the polymers made therein)" is meant a process which produces a polymer with a degree of polymerization (DP) of about 20 or more, preferably about 40 or more [except where otherwise noted, as in P in compound (VI)] By "DP" is meant the average number of repeat (monomer) units in the polymer.

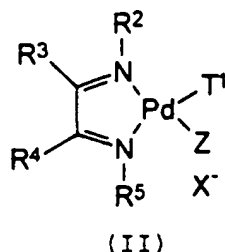
One of these catalysts may generally be written as



wherein: M is Ni(II), Co(II), Fe(II) or Pd(II); R<sup>2</sup> and R<sup>5</sup> are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; R<sup>3</sup> and R<sup>4</sup> are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R<sup>3</sup> and R<sup>4</sup> taken together are hydrocarbylene or substituted hydrocarbylene to form a ring; Q is alkyl, hydride, chloride, iodide, or bromide; and S is alkyl, hydride, chloride, iodide, or bromide. Preferably M is Ni(II) or Pd(II).

In a preferred form of (I), R<sup>3</sup> and R<sup>4</sup> are each independently hydrogen or hydrocarbyl. If Q and/or S is alkyl, it is preferred that the alkyl contains 1 to 4 carbon atoms, and more preferably is methyl.

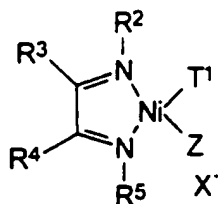
Another useful catalyst is



wherein:  $R^2$  and  $R^5$  are each independently hydrocarbyl  
 5 or substituted hydrocarbyl, provided that the carbon  
 atom bound to the imino nitrogen atom has at least two  
 carbon atoms bound to it;  $R^3$  and  $R^4$  are each  
 independently hydrogen, hydrocarbyl, substituted  
 hydrocarbyl or  $R^3$  and  $R^4$  taken together are  
 10 hydrocarbylene or substituted hydrocarbylene to form a  
 ring;  $T^1$  is hydrogen, hydrocarbyl not containing  
 olefinic or acetylenic bonds,  $R^{15}C(=O)-$  or  $R^{15}OC(=O)-$ ;  $Z$   
 is a neutral Lewis base wherein the donating atom is  
 nitrogen, sulfur or oxygen, provided that, if the  
 15 donating atom is nitrogen, then the  $pK_a$  of the  
 conjugate acid of that compound is less than about 6;  $X^-$   
 is a weakly coordinating anion; and  $R^{15}$  is hydrocarbyl  
 not containing olefinic or acetylenic bonds.

In one preferred form of (II),  $R^3$  and  $R^4$  are each  
 20 independently hydrogen or hydrocarbyl. In a more  
 preferred form of (II),  $T^1$  is alkyl, and  $T^1$  is  
 especially preferably methyl. It is preferred that  $Z$   
 is  $R^6_2O$  or  $R^7CN$ , wherein each  $R^6$  is independently  
 hydrocarbyl and  $R^7$  is hydrocarbyl. It is preferred that  
 25  $R^6$  and  $R^7$  are alkyl, and it is more preferred that they  
 are methyl or ethyl. It is preferred that  $X^-$  is  $BAF$ ,  
 $SbF_6$ ,  $PF_6$  or  $BF_4$ .

Another useful catalyst is



(III)

wherein:  $R^2$  and  $R^5$  are each independently hydrocarbyl  
 5 or substituted hydrocarbyl, provided that the carbon  
 atom bound to the imino nitrogen atom has at least two  
 carbon atoms bound to it;  $R^3$  and  $R^4$  are each  
 independently hydrogen, hydrocarbyl, or substituted  
 hydrocarbylene, or  $R^3$  and  $R^4$  taken together are  
 10 hydrocarbylene or substituted hydrocarbylene to form a  
 ring;  $T^1$  is hydrogen, hydrocarbyl not containing  
 olefinic or acetylenic bonds,  $R^{15}C(=O)-$  or  $R^{15}OC(=O)-$ ;  $Z$   
 is a neutral Lewis base wherein the donating atom is  
 nitrogen, sulfur or oxygen, provided that if the  
 15 donating atom is nitrogen then the  $pK_a$  of the conjugate  
 acid of that compound is less than about 6;  $X$  is a  
 weakly coordinating anion; and  $R^{15}$  is hydrocarbyl not  
 containing olefinic or acetylenic bonds.

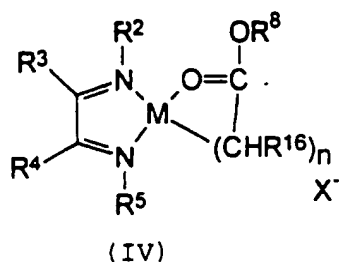
In one preferred form of (III),  $R^3$  and  $R^4$  are each  
 20 independently hydrogen, hydrocarbyl. In a more  
 preferred form of (III)  $T^1$  is alkyl, and  $T^1$  is  
 especially preferably methyl. It is preferred that  $Z$   
 is  $R^6_2O$  or  $R^7CN$ , wherein each  $R^6$  is independently  
 hydrocarbyl and  $R^7$  is hydrocarbyl. It is preferred  
 25 that  $R^6$  and  $R^7$  are alkyl, and it is especially preferred  
 that they are methyl or ethyl. It is preferred that  $X^-$   
 is  $BAF_4^-$ ,  $SbF_6^-$ ,  $PF_6^-$  or  $BF_4^-$ .

Relatively weakly coordinating anions are known to  
 the artisan. Such anions are often bulky anions,  
 30 particularly those that may delocalize their negative  
 charge. Suitable weakly coordinating anions in this  
 Application include  $(Ph)_4B^-$  ( $Ph$  = phenyl),  
 tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (herein



abbreviated BAF),  $\text{PF}_6^-$ ,  $\text{BF}_4^-$ ,  $\text{SbF}_6^-$ , trifluoromethanesulfonate, p-toluenesulfonate,  $(\text{R}_f\text{SO}_2)_2\text{N}^-$ , and  $(\text{C}_6\text{F}_5)_4\text{B}^-$ . Preferred weakly coordinating anions include  $\text{BAF}^-$ ,  $\text{PF}_6^-$ ,  $\text{BF}_4^-$ , and  $\text{SbF}_6^-$ .

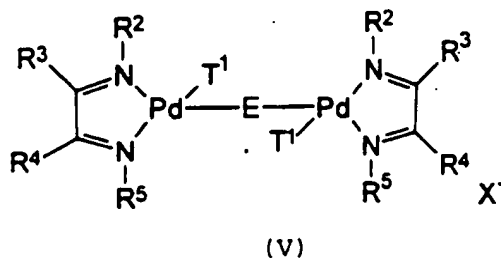
- 5 Also useful as a polymerization catalyst is a compound of the formula



- 10 wherein:  $\text{R}^2$  and  $\text{R}^5$  are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;  $\text{R}^3$  and  $\text{R}^4$  are each  
 15 independently hydrogen, hydrocarbyl, substituted hydrocarbyl or  $\text{R}^3$  and  $\text{R}^4$  taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;  $\text{M}$  is  $\text{Ni(II)}$  or  $\text{Pd(II)}$ ; each  $\text{R}^{16}$  is independently hydrogen or alkyl containing 1 to 10 carbon atoms;  $n$  is  
 20 1, 2, or 3;  $\text{X}$  is a weakly coordinating anion; and  $\text{R}^8$  is hydrocarbyl.

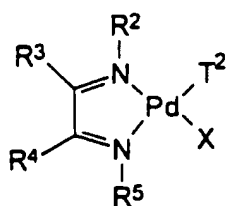
- It is preferred that  $n$  is 3, and all of  $\text{R}^{16}$  are hydrogen. It is also preferred that  $\text{R}^8$  is alkyl or substituted alkyl, especially preferred that it is  
 25 alkyl, and more preferred that  $\text{R}^8$  is methyl.

Another useful catalyst is



wherein:  $R^2$  and  $R^5$  are hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it;  $R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or  $R^3$  and  $R^4$  taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;  $T^1$  is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds,  $R^{15}C(=O)-$  or  $R^{15}OC(=O)-$ ;  $R^{15}$  is hydrocarbyl not containing olefinic or acetylenic bonds; E is halogen or  $-OR^{18}$ ;  $R^{18}$  is hydrocarbyl not containing olefinic or acetylenic bonds; and X is a weakly coordinating anion. It is preferred that  $T^1$  is alkyl containing 1 to 4 carbon atoms, and more preferred that it is methyl. In other preferred compounds (V),  $R^3$  and  $R^4$  are methyl or hydrogen and  $R^2$  and  $R^5$  are 2,6-diisopropylphenyl and X is BAF. It is also preferred that E is chlorine.

Another useful catalyst is a compound of the formula



(VII)

25

wherein:  $R^2$  and  $R^5$  are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;  $R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or  $R^3$  and  $R^4$  taken together are hydrocarbylene or substituted hydrocarbylene to form a

- ring;  $T^2$  is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, hydrocarbyl substituted with keto or ester groups but not containing olefinic or acetylenic bonds,  $R^{15}C(=O)-$  or  $R^{15}OC(=O)-$ ;  $R^{15}$  is
- 5 hydrocarbyl not containing olefinic or acetylenic bonds; and X is a weakly coordinating anion. In a more preferred form of (VII),  $T^2$  is alkyl containing 1 to 4 carbon atoms and  $T^2$  is especially preferably methyl. It is preferred that X is perfluoroalkylsulfonate,
- 10 especially trifluoromethanesulfonate (triflate). If  $X^-$  is an extremely weakly coordinating anion such as BAF, (VII) may not form. Thus it may be said that (VII) forms usually with weakly, but perhaps not extremely weakly, coordinating anions.
- 15 In all compounds, intermediates, catalysts, processes, etc. in which they appear it is preferred that  $R^2$  and  $R^5$  are each independently hydrocarbyl, and in one form it is especially preferred that  $R^2$  and  $R^5$  are both 2,6-diisopropylphenyl, particularly when  $R^3$
- 20 and  $R^4$  are each independently hydrogen or methyl. It is also preferred that  $R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl or taken together hydrocarbylene to form a carbocyclic ring.

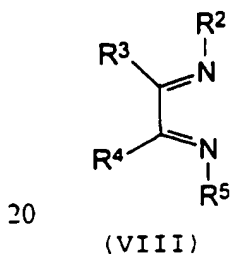
- Compounds of the formula (I) wherein M is Pd, Q is
- 25 alkyl and S is halogen may be made by the reaction of the corresponding 1,5-cyclooctadiene (COD) Pd complex with the appropriate diimine. When M is Ni, (I) can be made by the displacement of a another ligand, such as a dialkylether or a polyether such as 1,2-
- 30 dimethoxyethane, by an appropriate diimine.

- Catalysts of formula (II), wherein  $X^-$  is  $BAF^-$ , may be made by reacting a compound of formula (I) wherein Q is alkyl and S is halogen, with about one equivalent of an alkali metal salt, particularly the sodium salt, of
- 35 HBAF, in the presence of a coordinating ligand, particularly a nitrile such as acetonitrile. When  $X^-$  is an anion such as  $BAF^-$ ,  $SbF_6^-$  or  $BF_4^-$  the same

starting palladium compound can be reacted with the silver salt AgX.

However, sometimes the reaction of a diimine with a 1,5-COD Pd complex as described above to make compounds of formula (II) may be slow and/or give poor conversions, thereby rendering it difficult to make the starting material for (II) using the method described in the preceding paragraph. For instance when:  
 $R^2=R^5=Ph_2CH-$  and  $R^3=R^4=H$ ;  $R^2=R^5=Ph-$  and  $R^3=R^4=Ph$ ;  $R^2=R^5=2-$   
 10  $t$ -butylphenyl and  $R^3=R^4=CH_3$ ;  $R^2=R^5=\alpha$ -naphthyl and  $R^3=R^4=CH_3$ ; and  $R^2=R^5=2$ -phenylphenyl and  $R^3=R^4=CH_3$ , difficulty may be encountered in making a compound of formula (II).

In these instances it has been found more convenient to prepare (II) by reacting  $[(\eta^4-1,5-$   
 15  $COD)PdT^1Z] \cdot X^+$ , wherein  $T^1$  and  $X$  are as defined above and  $Z$  is an organic nitrile ligand, preferably in an organic nitrile solvent, with a diimine of the formula



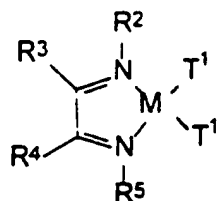
By a "nitrile solvent" is meant a solvent that is at least 20 volume percent nitrile compound. The product of this reaction is (II), in which the  $Z$  ligand is the nitrile used in the synthesis. In a preferred synthesis,  $T^1$  is methyl and the nitrile used is the same as in the starting palladium compound, and is more preferably acetonitrile. The process is carried out in solution, preferably when the nitrile is substantially all of the solvent, at a temperature of about  $-40^\circ C$  to about  $+60^\circ C$ , preferably about  $0^\circ C$  to about  $30^\circ C$ . It is

30

preferred that the reactants be used in substantially equimolar quantities.

The compound  $[(\eta^4\text{-}1,5\text{-COD})\text{PdT}^1\text{Z}]\text{X}^+$ , wherein  $\text{T}^1$  is alkyl, Z is an organic nitrile and X is a weakly coordinating anion may be made by the reaction of  $[(\eta^4\text{-}1,5\text{-COD})\text{PdT}^1\text{A}]$ , wherein A is Cl, Br or I and  $\text{T}^1$  is alkyl with the silver salt of  $\text{X}^-$ ,  $\text{AgX}$ , or if X is BAF with an alkali metal salt of HBAF, in the presence of an organic nitrile, which of course will become the ligand  $\text{T}^1$ . In a preferred process A is Cl,  $\text{T}^1$  is alkyl, more preferably methyl, and the organic nitrile is an alkyl nitrile, more preferably acetonitrile. The starting materials are preferably present in approximately equimolar amounts, except for the nitrile which is present preferably in excess. The solvent is preferably a non-coordinating solvent such as a halocarbon. Methylene chloride is useful as such a solvent. The process preferably is carried out at a temperature of about  $-40^\circ\text{C}$  to about  $+50^\circ\text{C}$ . It is preferred to exclude water and other hydroxyl containing compounds from the process, and this may be done by purification of the ingredients and keeping the process mass under an inert gas such as nitrogen.

Compounds of formula (II) [or (III) when the metal is nickel] can also be made by the reaction of

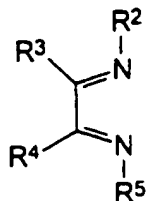


(X)

with a source of the conjugate acid of the anion X, the acid HX or its equivalent (such as a trityl salt) in the presence of a solvent which is a weakly coordinating ligand such as a dialkyl ether or an alkyl

nitrile. It is preferred to carry out this reaction at about  $-80^{\circ}\text{C}$  to about  $30^{\circ}\text{C}$ .

Compounds of formula (XXXXI) can be made by a process, comprising, contacting, at a temperature of about  $-80^{\circ}\text{C}$  to about  $+20^{\circ}\text{C}$ , a compound of the formula ( $\eta^4$ -1,5-COD)PdMe<sub>2</sub>, and a diimine of the formula



(VIII)

10

wherein: COD is 1,5-cyclooctadiene; R<sup>2</sup> and R<sup>5</sup> are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and R<sup>3</sup> and R<sup>4</sup> are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R<sup>3</sup> and R<sup>4</sup> taken together are hydrocarbylene or substituted hydrocarbylene to form a ring. It is preferred that the temperature is about  $-50^{\circ}\text{C}$  to about  $+10^{\circ}\text{C}$ . It is also preferred that the two starting materials be used in approximately equimolar quantities, and/or that the reaction be carried out in solution. It is preferred that R<sup>2</sup> and R<sup>5</sup> are both 2-t-butylphenyl or 2,5-di-t-butylphenyl and that R<sup>3</sup> and R<sup>4</sup> taken together are An, or R<sup>3</sup> and R<sup>4</sup> are both hydrogen or methyl.

Compounds of formula (IV) can be made by several routes. In one method a compound of formula (II) is reacted with an acrylate ester of the formula CH<sub>2</sub>=CHCO<sub>2</sub>R<sup>1</sup> wherein R<sup>1</sup> is as defined above. This reaction is carried out in a non-coordinating solvent such as methylene chloride, preferably using a greater than 1 to 50 fold excess of the acrylate ester. In a

- preferred reaction, Q is methyl, and R<sup>1</sup> is alkyl containing 1 to 4 carbon atoms, more preferably methyl. The process is carried out at a temperature of about -100°C to about +100°C, preferably about 0°C to about 50°C. It is preferred to exclude water and other hydroxyl containing compounds from the process, and this may be done by purification of the ingredients and keeping the process mass under an inert gas such as nitrogen
- 10 Alternatively, (IV) may be prepared by reacting (I), wherein Q is alkyl and S is Cl, Br or I with a source of an appropriate weakly coordinating anion such as AgX or an alkali metal salt of BAF and an acrylate ester (formula as immediately above) in a single step..
- 15 Approximately equimolar quantities of (I) and the weakly coordinating anion source are preferred, but the acrylate ester may be present in greater than 1 to 50 fold excess. In a preferred reaction, Q is methyl, and R<sup>1</sup> is alkyl containing 1 to 4 carbon atoms, more preferably methyl. The process is preferably carried out at a temperature of about -100°C to about +100°C, preferably about 0°C to about 50°C. It is preferred to exclude water and other hydroxyl containing compounds from the process, and this may be done by purification
- 20 of the ingredients and keeping the process mass under an inert gas such as nitrogen.

- In another variation of the preparation of (IV) from (I) the source of the weakly coordinating anion is a compound which itself does not contain an anion, but which can combine with S [of (I)] to form such a weakly coordinating anion. Thus in this type of process by "source of weakly coordinating anion" is meant a compound which itself contains the anion which will become X<sup>-</sup>, or a compound which during the process can
- 30 combine with other process ingredients to form such an anion.

Catalysts of formula (V), wherein X<sup>-</sup> is BAF<sup>-</sup>, may be made by reacting a compound of formula (I) wherein Q

is alkyl and S is halogen, with about one-half or an equivalent of an alkali metal salt, particularly the sodium salt, of HBAF. Alternatively, (V) containing other anions may be prepared by reacting (I), wherein Q is alkyl and S is Cl, Br or I with one-half equivalent of a source of an appropriate weakly coordinating anion such as AgX.

Some of the nickel and palladium compounds described above are useful in processes for polymerizing various olefins, and optionally also copolymerizing olefinic esters, carboxylic acids, or other functional olefins, with these olefins. When (I) is used as a catalyst, a neutral Lewis acid or a cationic Lewis or Bronsted acid whose counterion is a weakly coordinating anion is also present as part of the catalyst system (sometimes called a "first compound" in the claims). By a "neutral Lewis acid" is meant a compound which is a Lewis acid capable for abstracting  $Q^-$  or  $S^-$  from (I) to form a weakly coordination anion. The neutral Lewis acid is originally uncharged (i.e., not ionic). Suitable neutral Lewis acids include  $SbF_5$ ,  $Ar_3B$  (wherein Ar is aryl), and  $BF_3$ . By a cationic Lewis acid is meant a cation with a positive charge such as  $Ag^+$ ,  $H^+$ , and  $Na^+$ .

In those instances in which (I) (and similar catalysts which require the presence of a neutral Lewis acid or a cationic Lewis or Bronsted acid), does not contain an alkyl or hydride group already bonded to the metal (i.e., neither Q or S is alkyl or hydride), the neutral Lewis acid or a cationic Lewis or Bronsted acid also alkylates or adds a hydride to the metal, i.e., causes an alkyl group or hydride to become bonded to the metal atom.

A preferred neutral Lewis acid, which can alkylate the metal, is a selected alkyl aluminum compound, such as  $R^9_3Al$ ,  $R^9_2AlCl$ ,  $R^9AlCl_2$ , and " $R^9AlO$ " (alkylaluminoxanes), wherein  $R^9$  is alkyl containing 1 to 25 carbon atoms, preferably 1 to 4 carbon atoms.

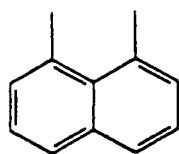


Suitable alkyl aluminum compounds include methylaluminumoxane (which is an oligomer with the general formula  $[\text{MeAlO}]_n$ ),  $(\text{C}_2\text{H}_5)_2\text{AlCl}$ ,  $\text{C}_2\text{H}_5\text{AlCl}_2$ , and  $[(\text{CH}_3)_2\text{CHCH}_2]_3\text{Al}$ .

5 Metal hydrides such as  $\text{NaBH}_4$  may be used to bond hydride groups to the metal M.

The first compound and (I) are contacted, usually in the liquid phase, and in the presence of the olefin, and/or 4-vinylcyclohexene, cyclopentene, cyclobutene, substituted norbornene, or norbornene. The liquid  
10 phase may include a compound added just as a solvent and/or may include the monomer(s) itself. The molar ratio of first compound:nickel or palladium complex is about 5 to about 1000, preferably about 10 to about  
15 100. The temperature at which the polymerization is carried out is about  $-100^\circ\text{C}$  to about  $+200^\circ\text{C}$ , preferably about  $-20^\circ\text{C}$  to about  $+80^\circ\text{C}$ . The pressure at which the polymerization is carried out is not critical, atmospheric pressure to about 275 MPa, or more, being a  
20 suitable range. The pressure may affect the microstructure of the polyolefin produced (see below).

When using (I) as a catalyst, it is preferred that  $\text{R}^3$  and  $\text{R}^4$  are hydrogen, methyl, or taken together are



25

(An)

It is also preferred that both  $\text{R}^2$  and  $\text{R}^5$  are 2,6-diisopropylphenyl, 2,6-dimethylphenyl, 2,6-diethylphenyl, 4-methylphenyl, phenyl, 2,4,6-trimethylphenyl, and 2-t-butylphenyl. When M is  
30  $\text{Ni(II)}$ , it is preferred that Q and S are each independently chloride or bromide, while when M is  $\text{Pd(II)}$  it is preferred that Q is methyl, chloride, or  
35 bromide, and S is chloride, bromide or methyl. In

addition, the specific combinations of groups in the catalysts listed in Table I are especially preferred.

Table I

5

R <sup>2</sup>	R <sup>3</sup>	R <sup>5</sup>	R <sup>5</sup>	Q	S	M
2,6-i-PrPh	H	H	2,6-i-PrPh	Me	Cl	Pd
2,6-i-PrPh	Me	Me	2,6-i-PrPh	Me	Cl	Pd
2,6-i-PrPh	An	An	2,6-i-PrPh	Me	Cl	Pd
2,6-MePh	H	H	2,6-MePh	Me	Cl	Pd
4-MePh	H	H	4-MePh	Me	Cl	Pd
4-MePh	Me	Me	4-MePh	Me	Cl	Pd
2,6-i-PrPh	Me	Me	2,6-i-PrPh	Me	Me	Pd
2,6-i-PrPh	H	H	2,6-i-PrPh	Me	Me	Pd
2,6-MePh	H	H	2,6-MePh	Me	Me	Pd
2,6-i-PrPh	H	H	2,6-i-PrPh	Br	Br	Ni
2,6-i-PrPh	Me	Me	2,6-i-PrPh	Br	Br	Ni
2,6-MePh	H	H	2,6-MePh	Br	Br	Ni
Ph	Me	Me	Ph	Me	Cl	Pd
2,6-EtPh	Me	Me	2,6-EtPh	Me	Cl	Pd
2,4,6-MePh	Me	Me	2,4,6-MePh	Me	Cl	Pd
2,6-MePh	Me	Me	2,6-MePh	Br	Br	Ni
2,6-i-PrPh	An	An	2,6-i-PrPh	Br	Br	Ni
2,6-MePh	An	An	2,6-MePh	Br	Br	Ni
2-t-BuPh	An	An	2-t-BuPh	Br	Br	Ni
2,5-t-BuPh	An	An	2,5-t-BuPh	Br	Br	Ni
2-i-Pr-6-MePh	An	An	2-i-Pr-6-MePh	Br	Br	Ni
2-i-Pr-6-MePh	Me	Me	2-i-Pr-6-MePh	Br	Br	Ni
2,6-t-BuPh	H	H	2,6-t-BuPh	Br	Br	Ni
2,6-t-BuPh	Me	Me	2,6-t-BuPh	Br	Br	Ni
2,6-t-BuPh	An	An	2,6-t-BuPh	Br	Br	Ni
2-t-BuPh	Me	Me	2-t-BuPh	Br	Br	Ni

Note - In Tables I and II, and elsewhere herein, the following convention and abbreviations are used. For R<sup>2</sup> and R<sup>5</sup>, when a substituted phenyl ring is present, the amount of substitution is indicated by the number of numbers indicating positions on the phenyl

ring, so that, for example, 2,6-i-PrPh is 2,6-diisopropylphenyl. The following abbreviations are used: i-Pr = isopropyl; Me = methyl; Et = ethyl; t-Bu = t-butyl; Ph = phenyl; Np = naphthyl; An = 1,8-naphthylidene (a divalent radical used for both R<sup>3</sup> and R<sup>4</sup>, wherein R<sup>3</sup> and R<sup>4</sup> taken together form a ring, which is part of an acenaphthylene group); OTf = triflate; and BAF = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate.

10

Preferred olefins in the polymerization are one or more of ethylene, propylene, 1-butene, 2-butene, 1-hexene 1-octene, 1-pentene, 1-tetradecene, norbornene, and cyclopentene, with ethylene, propylene and cyclopentene being more preferred. Ethylene (alone as a homopolymer) is especially preferred.

The polymerizations with (I) may be run in the presence of various liquids, particularly aprotic organic liquids. The catalyst system, monomer(s), and polymer may be soluble or insoluble in these liquids, but obviously these liquids should not prevent the polymerization from occurring. Suitable liquids include alkanes, cycloalkanes, selected halogenated hydrocarbons, and aromatic hydrocarbons. Specific useful solvents include hexane, toluene and benzene.

Whether such a liquid is used, and which and how much liquid is used, may affect the product obtained. It may affect the yield, microstructure, molecular weight, etc., of the polymer obtained.

Compounds of formulas (XI), (XIII), (XV) and (XIX) may also be used as catalysts for the polymerization of the same monomers as compounds of formula (I). The polymerization conditions are the same for (XI), (XIII), (XV) and (XIX) as for (I), and the same Lewis and Bronsted acids are used as co-catalysts. Preferred groupings R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, and R<sup>5</sup> (when present) in (XI) and (XIII) are the same as in (I), both in a polymerization process and as compounds in their own right.

Preferred (XI) compounds have the metals Sc(III), Zr(IV), Ni(II), Ni(I), Pd(II), Fe(II), and Co(II).

When M is Zr, Ti, Fe, and Sc it is preferred that all of Q and S are chlorine or bromine more preferably  
5 chlorine. When M is Ni or Co it is preferred that all of Q and S are chlorine, bromine or iodine, more preferably bromine.

In (XVII) preferred metals are Ni(II) and Ti(IV). It is preferred that all of Q and S are halogen. It is  
10 also preferred that all of  $R^{28}$ ,  $R^{29}$ , and  $R^{30}$  are hydrogen, and/or that both  $R^{44}$  and  $R^{45}$  are 2,4,6-trimethylphenyl or 9-anthracenyl.

In (XV) it is preferred that both of  $R^{31}$  are hydrogen.

15 In (XIII), (XXIII) and (XXXII) (as polymerization catalysts and as novel compounds) it is preferred that all of  $R^{20}$ ,  $R^{21}$ ,  $R^{22}$  and  $R^{23}$  are methyl. It is also preferred that  $T^1$  and  $T^2$  are methyl. For (XIII), when M is Ni(I) or (II), it is preferred that both Q and S  
20 are bromine, while when M is Pd it is preferred that Q is methyl and S is chlorine.

Compounds (II), (IV) or (VII) will each also cause the polymerization of one or more of an olefin, and/or a selected cyclic olefin such as cyclobutene,  
25 cyclopentene or norbornene, and, when it is a Pd(II) complex, optionally copolymerize an ester or carboxylic acid of the formula  $CH_2=CH(CH_2)_mCO_2R^1$ , wherein m is 0 or an integer of 1 to 16 and  $R^1$  is hydrogen or hydrocarbyl or substituted hydrocarbyl, by themselves (without  
30 cocatalysts). However, (III) often cannot be used when the ester is present. When norbornene or substituted norbornene is present no other monomer should be present.

Other monomers which may be used with compounds  
35 (II), (IV) or (VII) (when it is a Pd(II) complex) to form copolymers with olefins and selected cycloolefins are carbon monoxide (CO), and vinyl ketones of the general formula  $H_2C=CHC(O)R^{25}$ , wherein  $R^{25}$  is alkyl

containing 1 to 20 carbon atoms, and it is preferred that  $R^{25}$  is methyl. In the case of the vinyl ketones, the same compositional limits on the polymers produced apply as for the carboxylic acids and esters described as comonomers in the immediately preceding paragraph.

CO forms alternating copolymers with the various olefins and cycloolefins which may be polymerized with compounds (II), (IV) or (VII). The polymerization to form the alternating copolymers is done with both CO and the olefin simultaneously in the process mixture, and available to the catalyst. It is also possible to form block copolymers containing the alternating CO/(cyclo)olefin copolymers and other blocks containing just that olefin or other olefins or mixtures thereof. This may be done simply by sequentially exposing compounds (II), (IV) or (VII), and their subsequent living polymers, to the appropriate monomer or mixture of monomers to form the desired blocks. Copolymers of CO, a (cyclo)olefin and a saturated carboxylic acid or ester of the formula  $CH_2=CH(CH_2)_mCO_2R^1$ , wherein m is 0 or an integer of 1 to 16 and  $R^1$  is hydrogen or hydrocarbyl or substituted hydrocarbyl, may also be made by simultaneously exposing the polymerization catalyst or living polymer to these 3 types of monomers.

The polymerizations may be carried out with (II), (III), (IV) or (VII), and other catalyst molecules or combinations, initially in the solid state [assuming (II), (III) (IV) or (VII) is a solid] or in solution. The olefin and/or cycloolefin may be in the gas or liquid state (including gas dissolved in a solvent). A liquid, which may or may not be a solvent for any or all of the reactants and/or products may also be present. Suitable liquids include alkanes, cycloalkanes, halogenated alkanes and cycloalkanes, ethers, water, and alcohols, except that when (III) is used, hydrocarbons should preferably be used as solvents. Specific useful solvents include methylene

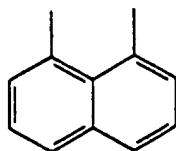
chloride, hexane, CO<sub>2</sub>, chloroform, perfluorō(n-butyltetrahydrofuran) (herein sometimes called FC-75), toluene, dichlorobenzene, 2-ethylhexanol, and benzene.

It is particularly noteworthy that one of the liquids which can be used in this polymerization process with (II), (III), (IV) or (VII) is water, see for instance Examples 213-216. Not only can water be present but the polymerization "medium" may be largely water, and various types of surfactants may be employed so that an emulsion polymerization may be done, along with a suspension polymerization when surfactants are not employed.

Preferred olefins and cycloolefins in the polymerization using (II), (III) or (IV) are one or more of ethylene, propylene, 1-butene, 1-hexene, 1-octene, 1-butene, cyclopentene, 1-tetradecene, and norbornene; and ethylene, propylene and cyclopentene are more preferred. Ethylene alone is especially preferred.

Olefinic esters or carboxylic acids of the formula  $\text{CH}_2=\text{CH}(\text{CH}_2)_m\text{CO}_2\text{R}^1$ , wherein  $\text{R}^1$  is hydrogen, hydrocarbyl, or substituted hydrocarbyl, and  $m$  is 0 or an integer of 1 to 16. It is preferred if  $\text{R}^1$  hydrocarbyl or substituted hydrocarbyl and it is more preferred if it is alkyl containing 1 to 10 carbon atoms, or glycidyl. It is also preferred if  $m$  is 0 and/or  $\text{R}^1$  is alkyl containing 1 to 10 carbon atoms. It is preferred to make copolymers containing up to about 60 mole percent, preferably up to about 20 mole percent of repeat units derived from the olefinic ester or carboxylic acid. Total repeat unit units in the polymer herein refer not only to those in the main chain from each monomer unit, but those in branches or side chains as well.

When using (II), (III), (IV) or (VII) as a catalyst it is preferred that  $\text{R}^3$  and  $\text{R}^4$  are hydrogen, methyl, or taken together are



(An)

It is also preferred that both  $R^2$  and  $R^5$  are 2,6-  
5 diisopropylphenyl, 2,6-dimethylphenyl, 4-methylphenyl,  
phenyl, 2,6-diethylphenyl, 2,4,6-trimethylphenyl and 2-  
t-butylphenyl. When (II) is used, it is preferred that  
 $T^1$  is methyl,  $R^6$  is methyl or ethyl and  $R^7$  is methyl.  
When (III) is used it is preferred that  $T^1$  is methyl  
10 and said Lewis base is  $R^6_2O$ , wherein  $R^6$  is methyl or  
ethyl. When (IV) is used it is preferred that  $R^8$  is  
methyl,  $n$  is 3 and  $R^{16}$  is hydrogen. In addition in  
Table II are listed all particularly preferred  
combinations as catalysts for (II), (III), (IV) and  
15 (VII).

Table II

Com- pound Type	R <sup>2</sup>	R <sup>1</sup>	R <sup>1</sup>	R <sup>5</sup>	T <sup>1</sup> /T <sup>2</sup> / R <sup>8</sup>	Z	M	X
(II)	2,6-i- PrPh	Me	Me	2,6-i- PrPh	Me	OEt <sub>2</sub>	Pd	BAF
(II)	2,6-i- PrPh	H	H	2,6-i- PrPh	Me	OEt <sub>2</sub>	Pd	BAF
(III)	2,6-i- PrPh	Me	Me	2,6-i- PrPh	Me	OEt <sub>2</sub>	Ni	BAF
(III)	2,6-i- PrPh	H	H	2,6-i- PrPh	Me	OEt <sub>2</sub>	Ni	BAF
(II)	2,6- MePh	H	H	2,6-MePh	Me	OEt <sub>2</sub>	Pd	BAF
(II)	2,6- MePh	Me	Me	2,6-MePh	Me	OEt <sub>2</sub>	Pd	BAF
(II)	2,6-i- PrPh	Me	Me	2,6-i- PrPh	Me	OEt <sub>2</sub>	Pd	SbF <sub>6</sub>
(II)	2,6-i- PrPh	Me	Me	2,6-i- PrPh	Me	OEt <sub>2</sub>	Pd	BF <sub>4</sub>
(II)	2,6-i- PrPh	Me	Me	2,6-i- PrPh	Me	OEt <sub>2</sub>	Pd	PF <sub>6</sub>
(II)	2,6-i- PrPh	H	H	2,6-i- PrPh	Me	OEt <sub>2</sub>	Pd	SbF <sub>6</sub>
(II)	2,4,6- MePh	Me	Me	2,4,6- MePh	Me	OEt <sub>2</sub>	Pd	SbF <sub>6</sub>
(II)	2,6-i- PrPh	An	An	2,6-i- PrPh	Me	OEt <sub>2</sub>	Pd	SbF <sub>6</sub>
(II)	2,6-i- PrPh	Me	Me	2,6-i- PrPh	Me	NCMe	Pd	SbF <sub>6</sub>
(II)	Ph	Me	Me	Ph	Me	NCMe	Pd	SbF <sub>6</sub>
(II)	2,6- EtPh	Me	Me	2,6-EtPh	Me	NCMe	Pd	BAF
(II)	2,6- EtPh	Me	Me	2,6-EtPh	Me	NCMe	Pd	SbF <sub>6</sub>
(II)	2-t- BuPh	Me	Me	2-t-BuPh	Me	NCMe	Pd	SbF <sub>6</sub>



(II)	1-Np	Me	Me	1-Np	Me	NCMe	Pd	SbF <sub>6</sub>
(II)	Ph <sub>2</sub> CH	H	H	Ph <sub>2</sub> CH	Me	NCMe	Pd	SbF <sub>6</sub>
(II)	2-PhPh	Me	Me	2-PhPh	Me	NCMe	Pd	SbF <sub>6</sub>
(II)	Ph	*	*	Ph	Me	NCMe	Pd	BAF
(IV)	2,6-i- PrPh	Me	Me	2,6-i- PrPh	Me	<sup>b</sup>	Pd	SbF <sub>6</sub>
(IV)	2,6-i- PrPh	Me	Me	2,6-i- PrPh	Me	<sup>b</sup>	Pd	BAF
(IV)	2,6-i- PrPh	H	H	2,6-i- PrPh	Me	<sup>b</sup>	Pd	SbF <sub>6</sub>
(IV)	2,6-i- PrPh	Me	Me	2,6-i- PrPh	Me	<sup>b</sup>	Pd	B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> C 1
(II)	Ph	Me	Me	Ph	Me	NCMe	Pd	SbF <sub>6</sub>
(VII)	2,6-i- PrPh	Me	Me	2,6-i- PrPh	Me	-	Pd	OTf
(II)	Ph	Ph	Ph	Ph	Me	NCMe	Pd	BAF
(II)	Ph <sub>2</sub> CH	H	H	Ph <sub>2</sub> CH	Me	NCMe	Pd	SbF <sub>6</sub>

\* This group is -CMe<sub>2</sub>CH<sub>2</sub>CMe<sub>2</sub>-

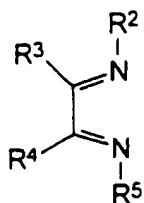
<sup>b</sup> This group is -(CH<sub>2</sub>)<sub>3</sub>CO<sub>2</sub>Me

When using (II), (III), (IV) or (VII) the  
 5 temperature at which the polymerization is carried out  
 is about -100°C to about +200°C, preferably about 0°C to  
 about 150°C, more preferably about 25°C to about 100°C.  
 The pressure at which the polymerization is carried out  
 is not critical, atmospheric pressure to about 275 MPa  
 10 being a suitable range. The pressure can affect the  
 microstructure of the polyolefin produced (see below).

Catalysts of the formulas (II), (III), (IV) and  
 (VII) may also be supported on a solid catalyst (as  
 opposed to just being added as a solid or in solution),  
 15 for instance on silica gel (see Example 98). By  
 supported is meant that the catalyst may simply be  
 carried physically on the surface of the solid support,  
 may be adsorbed, or carried by the support by other  
 means.

When using (XXX) as a ligand or in any process or reaction herein it is preferred that  $n$  is 2, all of  $R^{10}$ ,  $R^{28}$  and  $R^{29}$  are hydrogen, and both of  $R^{44}$  and  $R^{45}$  are 9-anthracenyl.

- 5 Another polymerization process comprises contacting a compound of the formula  $[Pd(R^{13}CN)_4]X_2$  or a combination of  $Pd[OC(O)R^{40}]_2$  and  $HX$ , with a compound of the formula



10

(VIII)

- and one or more monomers selected from the group consisting of ethylene, an olefin of the formula  $R^{17}CH=CH_2$  or  $R^{17}CH=CHR^{17}$ , cyclopentene, cyclobutene, substituted norbornene and norbornene, wherein:  $R^2$  and  $R^5$  are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;  $R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or  $R^3$  and  $R^4$  taken together are hydrocarbylene or substituted hydrocarbylene to form a carbocyclic ring; each  $R^{17}$  is independently hydrocarbyl or substituted hydrocarbyl provided that  $R^{17}$  contains no olefinic bonds;  $R^{40}$  is hydrocarbyl or substituted hydrocarbyl; and  $X$  is a weakly coordinating anion; provided that when norbornene or substituted norbornene is present no other monomer is present.

- 30 It is believed that in this process a catalyst similar to (II) may be initially generated, and this then causes the polymerization. Therefore, all of the conditions, monomers (including olefinic esters and

carboxylic acids), etc., which are applicable to the process using (II) as a polymerization catalyst are applicable to this process. All preferred items are also the same, including appropriate groups such as  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$ , and combinations thereof. This process however should be run so that all of the ingredients can contact each other, preferably in a single phase. Initially at least, it is preferred that this is done in solution. The molar ratio of (VIII) to palladium compound used is not critical, but for most economical use of the compounds, a moderate excess, about 25 to 100% excess, of (VIII) is preferably used.

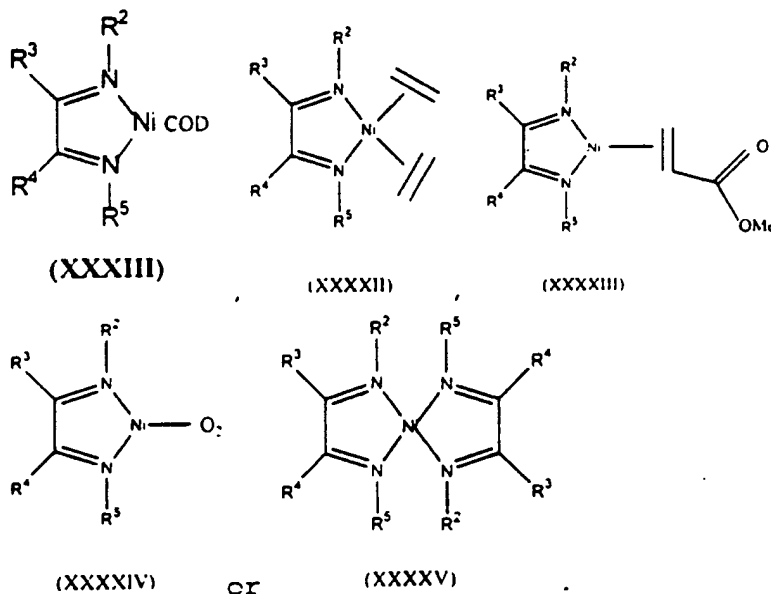
As mentioned above, it is believed that in the polymerization using (VIII) and  $[Pd(R^{13}CN)_4]X_2$  or a  $Pd[II]$  carboxylate a catalyst similar to (II) is formed. Other combinations of starting materials that can combine into catalysts similar to (II), (III), (IV) and (VII) often also cause similar polymerizations, see for instance Examples 238 and 239. Also combinations of  $\alpha$ -diimines or other diimino ligands described herein with: a nickel [0] or nickel [I] compound, oxygen, an alkyl aluminum compound and an olefin; a nickel [0] or nickel [I] compound, an acid such as HX and an olefin; or an  $\alpha$ -diimine Ni[0] or nickel [I] complex, oxygen, an alkyl aluminum compound and an olefin. Thus active catalysts from  $\alpha$ -diimines and other bidentate imino compounds can be formed beforehand or in the same "pot" (in situ) in which the polymerization takes place. In all of the polymerizations in which the catalysts are formed in situ, preferred groups on the  $\alpha$ -diimines are the same as for the preformed catalysts.

In general Ni[0], Ni[I] or Ni(II) compounds may be used as precursors to active catalyst species. They must have ligands which can be displaced by the appropriate bidentate nitrogen ligand, or must already contain such a bidentate ligand already bound to the nickel atom. Ligands which may be displaced include

1,5-cyclooctadiene and tris(o-tolyl)phosphite, which may be present in Ni[0] compounds, or dibenzylideneacetone, as in the useful Pd[0] precursor tris(dibenzylideneacetone)dipalladium[0]. These lower  
 5 valence nickel compounds are believed to be converted into active Ni[II] catalytic species. As such they must also be contacted (react with) with an oxidizing agent and a source of a weakly coordinating anion ( $X^-$ ). Oxidizing agents include oxygen, HX (wherein X is a  
 10 weakly coordinating anion), and other well known oxidizing agents. Sources of  $X^-$  include HX, alkylaluminum compounds, alkali metal and silver salts of  $X^-$ . As can be seen above, some compounds such as HX may act as both an oxidizing agent and a source of  $X^-$ .  
 15 Compounds containing other lower valent metals may be converted into active catalyst species by similar methods.

When contacted with an alkyl aluminum compound or HX useful Ni[0] compounds include

20



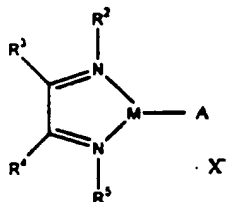
Various types of Ni[0] compounds are known in the literature. Below are listed references for the types  
 25 shown immediately above.

- (XXXIII) G. van Koten, et al., *Adv. Organometal. Chem.*, vol. 21, p. 151-239 (1982).
- (XXXXII) W. Bonrath, et al., *Angew. Chem. Int. Ed. Engl.*, vol. 29, p. 298-300 (1990).
- 5 • (XXXXIV) H. tom Dieck, et al., *Z. Naturforsch.*, vol. 366, p. 823-832 (1981); and M. Svoboda, et al., *J. Organometal. Chem.*, vol. 191, p. 321-328 (1980).
- (XXXXV) G. van Koten, et al., *Adv. Organometal. Chem.*, vol. 21, p. 151-239 (1982).

In polymerizations using (XIV), the same preferred monomers and groups (such as  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$  and X) as are preferred for the polymerization using (II) are used and preferred. Likewise, the conditions used and preferred for polymerizations with (XIV) are similar to those used and preferred for (II), except that higher olefin pressures (when the olefin is a gas) are preferred. Preferred pressures are about 2.0 to about 20 MPa. (XIV) may be prepared by the reaction of one mole of  $[Pd(R^{13}CN)_4]X_2$  with one mole of (VIII) in acetonitrile or nitromethane.

Novel compound (XIV) is used as an olefin polymerization catalyst. In preferred forms of (XIV), the preferred groups  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$  and X are the same as are preferred for compound (II).

Another type of compound which is an olefin polymerization catalyst are  $\pi$ -allyl and  $\pi$ -benzyl compounds of the formula



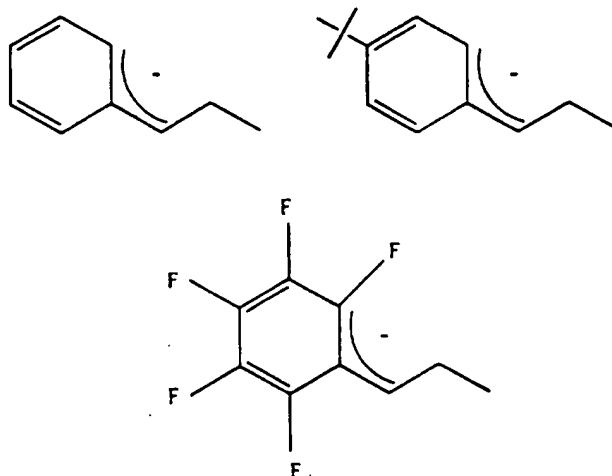
### XXXVII

- wherein M is Ni(II) or Pd(II);  $R^2$  and  $R^5$  are hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen

atom has at least two carbon atoms bound to it;  $R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or  $R^3$  and  $R^4$  taken together are hydrocarbylene or substituted hydrocarbylene to form a  
 5 ring; X is a weakly coordinating anion; and A is a  $\pi$ -allyl or  $\pi$ -benzyl group. By a  $\pi$ -allyl group is meant a monoanionic with 3 adjacent  $sp^2$  carbon atoms bound to a metal center in an  $\eta^3$  fashion. The three  $sp^2$  carbon atoms may be substituted with other hydrocarbyl groups  
 10 or functional groups. Typical  $\pi$ -allyl groups include



wherein R is hydrocarbyl. By a  $\pi$ -benzyl group is meant  
 15  $\pi$ -allyl ligand in which two of the  $sp^2$  carbon atoms are part of an aromatic ring. Typical  $\pi$ -benzyl groups include



20

$\pi$ -Benzyl compounds usually initiate polymerization of the olefins fairly readily even at room temperature, but  $\pi$ -allyl compounds may not necessarily do so.

Initiation of  $\pi$ -allyl compounds can be improved by using one or more of the following methods:

- Using a higher temperature such as about 80°C.

5       • Decreasing the bulk of the  $\alpha$ -diimine ligand, such as R<sup>2</sup> and R<sup>5</sup> being 2,6-dimethylphenyl instead of 2,6-diisopropylphenyl.

- Making the  $\pi$ -allyl ligand more bulky, such as using

10

  
rather than the simple  $\pi$ -allyl group itself.

- Having a Lewis acid present while using a functional  $\pi$ -allyl or  $\pi$ -benzyl group. Relatively weak

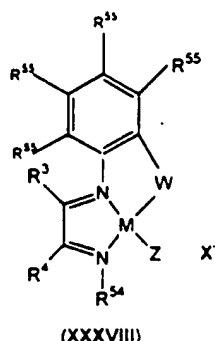
15 Lewis acids such as triphenylborane, tris(pentafluorophenyl)borane, and tris(3,5-trifluoromethylphenyl)borane, are preferred. Suitable functional groups include chloro and ester. "Solid" acids such as montmorillonite may also be used.

20       When using (XXXVII) as a polymerization catalyst, it is preferred that ethylene and/or a linear  $\alpha$ -olefin is the monomer, or cyclopentene, more preferred if the monomer is ethylene and/or propylene, and ethylene is especially preferred. A preferred temperature for the

25 polymerization process using (XXXVII) is about +20°C to about 100°C. It is also preferred that the partial pressure due to ethylene or propylene monomer is at least about 600 kPa. It is also noted that (XXXVII) is a novel compound, and preferred items for (XXXVII) for

30 the polymerization process are also preferred for the compound itself.

Another catalyst for the polymerization of olefins is a compound of the formula



- and one or more monomers selected from the group consisting of ethylene, an olefin of the formula  $R^{17}CH=CH_2$  or  $R^{17}CH=CHR^{17}$ , cyclobutene, cyclopentene,
- 5 substituted norbornene, and norbornene,
- wherein:  $R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or  $R^3$  and  $R^4$  taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;  $R^{54}$  is hydrocarbyl or
- 10 substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it; each  $R^{55}$  is independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or a functional group; W is alkylene or substituted alkylene
- 15 containing 2 or more carbon atoms; Z is a neutral Lewis base wherein the donating atom is nitrogen, sulfur, or oxygen, provided that if the donating atom is nitrogen then the pKa of the conjugate acid of that compound (measured in water) is less than about 6, or an olefin
- 20 of the formula  $R^{17}CH=CHR^{17}$ ; each  $R^{17}$  is independently alkyl or substituted alkyl; and X is a weakly coordinating anion. It is preferred that in compound (XXXVIII) that:  $R^{54}$  is phenyl or substituted phenyl, and preferred substituents are alkyl groups; each  $R^{55}$  is
- 25 independently hydrogen or alkyl containing 1 to 10 carbon atoms; W contains 2 carbon atoms between the phenyl ring and metal atom it is bonded to or W is a divalent polymeric group derived from the polymerization of  $R^{17}CH=CHR^{17}$ , and it is especially
- 30 preferred that it is  $-CH(CH_3)CH_2-$  or  $-C(CH_3)_2CH_2-$ ; and Z is a dialkyl ether or an olefin of the formula



$R^{17}CH=CHR^{17}$ ; and combinations thereof. W is an alkylene group in which each of the two free valencies are to different carbon atoms of the alkylene group.

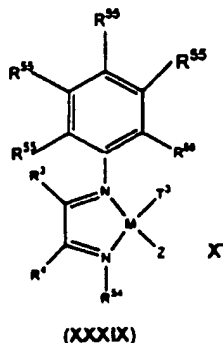
When W is a divalent group formed by the polymerization of  $R^{17}CH=CHR^{17}$ , and Z is  $R^{17}CH=CHR^{17}$ , the compound (XXXVIII) is believed to be a living ended polymer. That end of W bound to the phenyl ring actually is the original fragment from  $R^{56}$  from which the "bridge" W originally formed, and the remaining part of W is formed from the olefin(s)  $R^{17}CH=CHR^{17}$ . In a sense this compound is similar in function to compound (VI).

By substituted phenyl in (XXXVIII) and (XXXIX) is meant the phenyl ring can be substituted with any grouping which does not interfere with the compound's stability or any of the reactions the compound undergoes. Preferred substituents in substituted phenyl are alkyl groups, preferably containing 1 to 10 carbon atoms.

Preferred monomers for this polymerization are ethylene and linear  $\alpha$ -olefins, or cyclopentene, particularly propylene, and ethylene and propylene or both are more preferred, and ethylene is especially preferred.

It is noted that (XXXVIII) is a novel compound, and preferred compounds and groupings are the same as in the polymerization process.

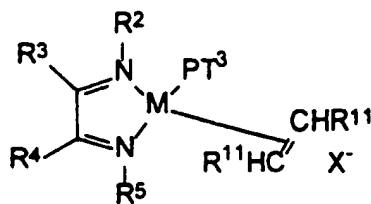
Compound (XXXVIII) can be made by heating compound (XXXIX),



wherein:  $R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or  $R^3$  and  $R^4$  taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;  $R^{54}$  is hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it; each  $R^{55}$  is independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or a functional group;  $R^{56}$  is alkyl containing 2 to 30 carbon atoms;  $T^3$  is alkyl; Z is a neutral Lewis base wherein the donating atom is nitrogen, sulfur, or oxygen, provided that if the donating atom is nitrogen then the pKa of the conjugate acid of that compound (measured in water) is less than about 6; and X is a weakly coordinating anion. Preferred groups are the same as those in (XXXVIII). In addition it is preferred that  $T^5$  contain 1 to 10 carbon atoms, and more preferred that it is methyl. A preferred temperature for the conversion of (XXXIX) to (XXXVIII) is about  $-30^{\circ}\text{C}$  to about  $50^{\circ}\text{C}$ . Typically the reaction takes about 10 min. to about 5 days, the higher the temperature, the faster the reaction. Another factor which affects the reaction rate is the nature of Z. The weaker the Lewis basicity of Z, the faster the desired reaction will be.

When (II), (III), (IV), (V), (VII), (VIII) or a combination of compounds that will generate similar compounds, (subject to the conditions described above) is used in the polymerization of olefins, cycloolefins, and optionally olefinic esters or carboxylic acids, polymer having what is believed to be similar to a "living end" is formed. This molecule is that from which the polymer grows to its eventual molecular weight. This compound may have the structure

35



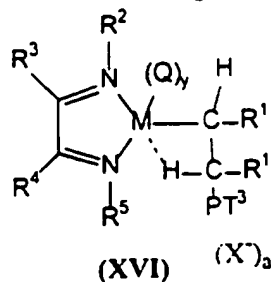
- wherein: M is Ni(II) or Pd(II); R<sup>2</sup> and R<sup>5</sup> are
- 5 hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it; R<sup>3</sup> and R<sup>4</sup> are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R<sup>3</sup> and R<sup>4</sup> taken together are
- 10 hydrocarbylene or substituted hydrocarbylene to form a ring; each R<sup>11</sup> is independently hydrogen, alkyl or -(CH<sub>2</sub>)<sub>m</sub>CO<sub>2</sub>R<sup>1</sup>; T<sup>3</sup> is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, R<sup>15</sup>(C=O)-, R<sup>15</sup>O(C=O)-, or -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>R<sup>8</sup>; R<sup>15</sup> is hydrocarbyl not containing
- 15 olefinic or acetylenic unsaturation; P is a divalent group containing one or more repeat units derived from the polymerization of one or more of ethylene, an olefin of the formula R<sup>17</sup>CH=CH<sub>2</sub> or R<sup>17</sup>CH=CHR<sup>17</sup>, cyclobutene, cyclopentene, substituted norbornene, or
- 20 norbornene and, when M is Pd(II), optionally one or more compounds of the formula CH<sub>2</sub>=CH(CH<sub>2</sub>)<sub>m</sub>CO<sub>2</sub>R<sup>1</sup>; R<sup>8</sup> is hydrocarbyl; each R<sup>17</sup> is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic
- 25 bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms; m is 0 or an integer from 1 to 16; R<sup>1</sup> is hydrogen, or hydrocarbyl or substituted hydrocarbyl containing 1 to 10 carbon atoms; and X is a weakly coordinating anion; and that
- 30 when M is Ni(II), R<sup>11</sup> is not -CO<sub>2</sub>R<sup>8</sup> and when M is Pd a diene is not present. By an "olefinic ester or carboxylic acid" is meant a compound of the formula

$\text{CH}_2=\text{CH}(\text{CH}_2)_m\text{CO}_2\text{R}^1$ , wherein  $m$  and  $\text{R}^1$  are as defined immediately above.

This molecule will react with additional monomer (olefin, cyclic olefin, olefinic ester or olefinic carboxylic acid) to cause further polymerization. In other words, the additional monomer will be added to P, extending the length of the polymer chain. Thus P may be of any size, from one "repeat unit" to many repeat units, and when the polymerization is over and P is removed from M, as by hydrolysis, P is essentially the polymer product of the polymerization. Polymerizations with (VI), that is contact of additional monomer with this molecule takes place under the same conditions as described above for the polymerization process using (II), (III), (IV), (V), (VII) or (VIII), or combinations of compounds that will generate similar molecules, and where appropriate preferred conditions and structures are the same.

The group  $\text{T}^3$  in (VI) was originally the group  $\text{T}^1$  in (II) or (III), or the group which included  $\text{R}^8$  in (IV). It in essence will normally be one of the end groups of the eventual polymer product. The olefinic group which is coordinated to M,  $\text{R}^{11}\text{CH}=\text{CHR}^{11}$  is normally one of the monomers, olefin, cyclic olefin, or, if  $\text{Pd(II)}$  is M, an olefinic ester or carboxylic acid. If more than one of these monomers is present in the reaction, it may be any one of them. It is preferred that  $\text{T}^3$  is alkyl and especially preferred that it is methyl, and it is also preferred that  $\text{R}^{11}$  is hydrogen or n-alkyl. It is also preferred that M is  $\text{Pd(II)}$ .

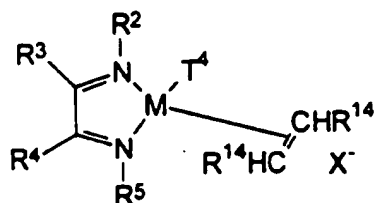
Another "form" for the living end is (XVI).



This type of compound is sometimes referred to as a compound in the "agostic state". In fact both (VI) and (XVI) may coexist together in the same polymerization, both types of compound representing living ends. It is believed that (XVI)-type compounds are particularly favored when the end of the growing polymer chain bound to the transition metal is derived from a cyclic olefin such as cyclopentene. Expressed in terms of the structure of (XVI) this is when both of  $R^{11}$  are hydrocarbylene to form a carbocyclic ring, and it is preferred that this be a five-membered carbocyclic ring.

For both the polymerization process using (XVI) and the structure of (XVI) itself, the same conditions and groups as are used and preferred for (VI) are also used and preferred for (XVI), with the exception that for  $R^{11}$  it is preferred in (XVI) that both of  $R^{11}$  are hydrocarbylene to form a carbocyclic ring.

This invention also concerns a compound of the formula



(IX)

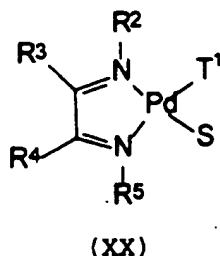
wherein: M is Ni(II) or Pd(II);  $R^2$  and  $R^5$  are hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it;  $R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or  $R^3$  and  $R^4$  taken together are hydrocarbylene or substituted hydrocarbylene to form a

ring; each  $R^{14}$  is independently hydrogen, alkyl or  
[when M is Pd(II)]  $-(CH_2)_mCO_2R^1$ ;  $R^1$  is hydrogen, or  
hydrocarbyl or substituted hydrocarbyl containing 1 to  
10 carbon atoms;  $T^4$  is alkyl,  $-R^{60}C(O)OR^8$ ,  $R^{15}(C=O)-$  or  
5  $R^{15}OC(=O)-$ ;  $R^{15}$  is hydrocarbyl not containing olefinic  
or acetylenic bonds;  $R^{60}$  is alkylene not containing  
olefinic or acetylenic bonds;  $R^8$  is hydrocarbyl; and X  
is a weakly coordinating anion.

(IX) may also be used to polymerize olefins,  
10 cyclic olefins, and optionally olefinic esters and  
carboxylic acids. The same conditions (except as noted  
below) apply to the polymerizations using (IX) as they  
do for (VI). It is preferred that M is Pd(II) and  $T^4$   
is methyl.

15 A compound of formula (V) may also be used as a  
catalyst for the polymerization of olefins, cyclic  
olefins, and optionally olefinic esters and/or  
carboxylic acids. In this process (V) is contacted  
with one or more of the essential monomers. Optionally  
20 a source of a relatively weakly coordinating anion may  
also be present. Such a source could be an alkali  
metal salt of BAF or AgX (wherein X is the anion), etc.  
Preferably about 1 mole of the source of X, such as  
AgX, will be added per mole of (V). This will usually  
25 be done in the liquid phase, preferably in which (V)  
and the source of the anion are at least partially  
soluble. The conditions of this polymerization are  
otherwise the same as described above for (II), (III),  
(IV) and (VII), including the preferred conditions and  
30 ingredients.

In polymerizations using (XX) as the catalyst,  
a first compound which is a source of a relatively  
noncoordinating monoanion is present. Such a source  
can be an alkali metal or silver salt of the monoanion.  
35



It is preferred that the alkali metal cation is sodium  
 5 or potassium. It is preferred that the monoanion is  $\text{SbF}_6^-$ ,  $\text{BAF}$ ,  $\text{PF}_6^-$ , or  $\text{BF}_4^-$ , and more preferred that it is  $\text{BAF}$ . It is preferred that  $\text{T}^1$  is methyl and/or S is chlorine. All other preferred groups and conditions  
 10 for these polymerizations are the same as for polymerizations with (II).

In all of the above polymerizations, and the  
 catalysts for making them it is preferred that  $\text{R}^2$  and  
 $\text{R}^5$ , if present, are 2,6-diisopropylphenyl and  $\text{R}^3$  and  $\text{R}^4$   
 are hydrogen or methyl. When cyclopentene is  
 15 polymerized, is preferred that  $\text{R}^2$  and  $\text{R}^5$  (if present)  
 are 2,6-dimethylphenyl or 2,4,6-trimethylphenyl and  
 that  $\text{R}^3$  and  $\text{R}^4$  taken together are An.  $\text{R}^2$ ,  $\text{R}^3$ ,  $\text{R}^4$  and  $\text{R}^5$   
 and other groups herein may also be substituted  
 hydrocarbyl. As previously defined, the substituent  
 20 groups in substituted hydrocarbyl groups (there may be  
 one or more substituent groups) should not  
 substantially interfere with the polymerization or  
 other reactions that the compound is undergoing.  
 Whether a particular group will interfere can first be  
 25 judged from the artisans general knowledge and the  
 particular polymerization or other reaction that is  
 involved. For instance, in polymerizations where an  
 alkyl aluminum compound is used may not be compatible  
 with the presence of groups containing an active  
 30 (relatively acidic) hydrogen atom, such as hydroxyl or  
 carboxyl because of the known reaction of alkyl  
 aluminum compounds with such active hydrogen containing  
 groups (but such polymerizations may be possible if

enough "extra" alkyl aluminum compound is added to react with these groups). However, in very similar polymerizations where alkyl aluminum compounds are not present, these groups containing active hydrogen may be present. Indeed many of the polymerization processes described herein are remarkably tolerant to the presence of various functional groups. Probably the most important considerations as to the operability of compounds containing any particular functional group are the effect of the group on the coordination of the metal atom (if present), and side reaction of the group with other process ingredients (such as noted above). Therefore of course, the further away from the metal atom the functional group is, the less likely it is to influence, say, a polymerization. If there is doubt as to whether a particular functional group, in a particular position, will affect a reaction, simple minimal experimentation will provide the requisite answer. Functional groups which may be present in  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$ , and other similar radicals herein include hydroxy, halo (fluoro, chloro, bromo and iodo), ether, ester, dialkylamino, carboxy, oxo (keto and aldehydo), nitro, amide, thioether, and imino. Preferred functional groups are hydroxy, halo, ether and dialkylamino.

Also in all of the polymerizations, the (cyclo)olefin may be substituted hydrocarbyl. Suitable substituents include ether, keto, aldehyde, ester, carboxylic acid.

In all of the above polymerizations, with the exceptions noted below, the following monomer(s), to produce the corresponding homo- or copolymers, are preferred to be used: ethylene; propylene; ethylene and propylene; ethylene and an  $\alpha$ -olefin; an  $\alpha$ -olefin; ethylene and an alkyl acrylate, especially methyl acrylate; ethylene and acrylic acid; ethylene and carbon monoxide; ethylene, and carbon monoxide and an acrylate ester or acrylic acid, especially methyl



acrylate; propylene and alkyl acrylate, especially methyl acrylate; cyclopentene; cyclopentene and ethylene; cyclopentene and propylene. Monomers which contain a carbonyl group, including esters, carboxylic acids, carbon monoxide, vinyl ketones, etc., can be polymerized with Pd(II) containing catalysts herein, with the exception of those that require the presence of a neutral or cationic Lewis acid or cationic Bronsted acid, which is usually called the "first compound" in claims describing such polymerization processes.

Another useful "monomer" for these polymerization processes is a C<sub>4</sub> refinery catalytic cracker stream, which will often contain a mixture of n-butane, isobutane, isobutene, 1-butene, 2-butenes and small amounts of butadiene. This type of stream is referred to herein as a "crude butenes stream". This stream may act as both the monomer source and "solvent" for the polymerization. It is preferred that the concentration of 1- and 2-butenes in the stream be as high as possible, since these are the preferred compounds to be polymerized. The butadiene content should be minimized because it may be a polymerization catalyst poison. The isobutene may have been previously removed for other uses. After being used in the polymerization (during which much or most of the 1-butene would have been polymerized), the butenes stream can be returned to the refinery for further processing.

In many of the these polymerizations certain general trends may be noted, although for all of these trends there are exceptions. These trends (and exceptions) can be gleaned from the Examples.

Pressure of the monomers (especially gaseous monomers such as ethylene) has an effect on the polymerizations in many instances. Higher pressure often affects the polymer microstructure by reducing branching, especially in ethylene containing polymers. This effect is more pronounced for Ni catalysts than Pd

catalysts. Under certain conditions higher pressures also seem to give higher productivities and higher molecular weight. When an acrylate is present and a Pd catalyst is used, increasing pressure seems to decrease the acrylate content in the resulting copolymer.

Temperature also affects these polymerizations. Higher temperature usually increases branching with Ni catalysts, but often has little such effect using Pd catalysts. With Ni catalysts, higher temperatures appear to often decrease molecular weight. With Pd catalysts, when acrylates are present, increasing temperature usually increases the acrylate content of the polymer, but also often decreases the productivity and molecular weight of the polymer.

Anions surprisingly also often affect molecular weight of the polymer formed. More highly coordinating anions often give lower molecular weight polymers. Although all of the anions useful herein are relatively weakly coordinating, some are more strongly coordinating than others. The coordinating ability of such anions is known and has been discussed in the literature, see for instance W. Beck., et al., Chem. Rev., vol. 88 p. 1405-1421 (1988), and S. H. Strauss, Chem. Rev., vol. 93, p. 927-942 (1993), both of which are hereby included by reference. The results found herein in which the molecular weight of the polymer produced is related to the coordinating ability of the anion used, is in line with the coordinating abilities of these anions as described in Beck (p. 1411) and Strauss (p. 932, Table II).

In addition to the "traditional" weakly coordinating anions cited in the paragraph immediately above, heterogeneous anions may also be employed. In these cases, the true nature of the counterion is poorly defined or unknown. Included in this group are MAO, MMAO and related aluminoxanes which do not form true solutions. The resulting counterions are thought to bear anionic aluminate moieties related to those

cited in the paragraph immediately above. Polymeric anionic materials such as Nafion<sup>®</sup> polyfluorosulfonic acid can function as non-coordinating counterions. In addition, a wide variety of heterogeneous inorganic materials can be made to function as non-coordinating counterions. Examples would include aluminas, silicas, silica/aluminas, cordierites, clays,  $MgCl_2$ , and many others utilized as traditional supports for Ziegler-Natta olefin polymerization catalysts. These are generally materials which have Lewis or Bronsted acidity. High surface area is usually desired and often these materials will have been activated through some heating process. Heating may remove excess surface water and change the surface acidity from Bronsted to Lewis type. Materials which are not active in the role may often be made active by surface treatment. For instance, a surface-hydrated silica, zinc oxide or carbon can be treated with an organoaluminum compound to provide the required functionality.

The catalysts described herein can be heterogenized through a variety of means. The heterogeneous anions in the paragraph immediately above will all serve to heterogenize the catalysts. Catalysts can also be heterogenized by exposing them to small quantities of a monomer to encapsulate them in a polymeric material through which additional monomers will diffuse. Another method is to spray-dry the catalyst with its suitable non-coordinating counterion onto a polymeric support. Heterogeneous versions of the catalyst are particularly useful for running gas-phase polymerizations. The catalyst is suitably diluted and dispersed on the surface of the catalyst support to control the heat of polymerization. When applied to fluidized-bed polymerizations, the heterogeneous supports provide a convenient means of catalyst introduction.

Anions have been found to have another unexpected effect. They can effect the amount of incorporation of an acrylic monomer such as an ester into an olefin/acrylic copolymer. For instance it has been  
5 found that  $\text{SbF}_6^-$  anion incorporates more fluorinated alkyl acrylate ester into an ethylene copolymer than BAF anion, see for instance Example 302.

Another item may effect the incorporation of polar monomers such as acrylic esters in olefin copolymers.  
10 It has been found that catalysts containing less bulky  $\alpha$ -diimines incorporate more of the polar monomer into the polymer (one obtains a polymer with a higher percentage of polar monomer) than a catalyst containing a more bulky  $\alpha$ -diimine, particularly when ethylene is  
15 the olefin comonomer. For instance, in an  $\alpha$ -diimine of formula (VIII), if  $\text{R}^2$  and  $\text{R}^5$  are 2,6-dimethylphenyl instead of 2,6-diisopropylphenyl, more acrylic monomer will be incorporated into the polymer. However, another common effect of using a less bulky catalyst is  
20 to produce a polymer with lower molecular weight. Therefore one may have to make a compromise between polar monomer content in the polymer and polymer molecular weight.

When an olefinic carboxylic acid is polymerized  
25 into the polymer, the polymer will of course contain carboxyl groups. Similarly in an ester containing polymer, some or all of the ester groups may be hydrolyzed to carboxyl groups (and vice versa). The carboxyl groups may be partially or completely  
30 converted into salts such as metallic salts. Such polymeric salts are termed ionomers. Ionomers are useful in adhesives, as ionomeric elastomers, and as molding resins. Salts may be made with ions of metals such as Na, K, Zn, Mg, Al, etc. The polymeric salts  
35 may be made by methods known to the artisan, for instance reaction of the carboxylic acid containing polymers with various compounds of the metals such as bases (hydroxides, carbonates, etc.) or other

compounds, such as acetylacetonates. Novel polymers that contain carboxylic acid groups herein, also form novel ionomers when the carboxylic acid groups are partially or fully converted to carboxylate salts.

5 When copolymers of an olefinic carboxylic acid or olefinic ester and selected olefins are made, they may be crosslinked by various methods known in the art, depending on the specific monomers used to make the polymer. For instance, carboxyl or ester containing  
10 polymers may be crosslinked by reaction with diamines to form bisamides. Certain functional groups which may be present on the polymer may be induced to react to crosslink the polymer. For instance epoxy groups (which may be present as glycidyl esters) may be  
15 crosslinked by reaction of the epoxy groups, see for instance Example 135.

It has also been found that certain fluorinated olefins, some of them containing other functional groups may be polymerized by nickel and palladium  
20 catalysts. Note that these fluorinated olefins are included within the definition of  $H_2C=CHR^{17}$ , wherein  $R^{17}$  can be considered to be substituted hydrocarbyl, the substitution being fluorine and possibly other substituents. Olefins which may be polymerized include  
25  $H_2C=CH(CH_2)_aR^{42}$  wherein  $a$  is an integer of 2 to 20,  $R_f$  is perfluoroalkylene optionally containing one or more ether groups, and  $R^{42}$  is fluorine or a functional group. Suitable functional groups include hydrogen, chlorine, bromine or iodine, ester, sulfonic acid ( $-SO_3H$ ), and sulfonyl halide. Preferred groups for  $R^{42}$   
30 include fluorine, ester, sulfonic acid, and sulfonyl fluoride. A sulfonic acid group containing monomer does not have to be polymerized directly. It is preferably made by hydrolysis of a sulfonyl halide group already present in an already made polymer. It  
35 is preferred that the perfluoroalkylene group contain 2 to 20 carbon atoms and preferred perfluoroalkylene groups are  $-(CF_2)_b-$  wherein  $b$  is 2 to 20, and -

(CF<sub>2</sub>)<sub>d</sub>OCF<sub>2</sub>CF<sub>2</sub>- wherein d is 2 to 20. A preferred olefinic comonomer is ethylene or a linear α-olefin, and ethylene is especially preferred. Polymerizations may be carried out with many of the catalysts described  
5 herein, see Examples 284 to 293.

As described herein, the resulting fluorinated polymers often don't contain the expected amount of branching, and/or the lengths of the branches present are not those expected for a simple vinyl  
10 polymerization.

The resulting polymers may be useful for compatibilizing fluorinated and nonfluorinated polymers, for changing the surface characteristics of fluorinated or nonfluorinated polymers (by being mixed  
15 with them), as molding resins, etc. Those polymers containing functional groups may be useful where those functional groups may react or be catalysts. For instance, if a polymer is made with a sulfonyl fluoride group (R<sup>42</sup> is sulfonyl fluoride) that group may be  
20 hydrolyzed to a sulfonic acid, which being highly fluorinated is well known to be a very strong acid. Thus the polymer may be used as an acid catalyst, for example for the polymerization of cyclic ethers such as tetrahydrofuran.

25 In this use it has been found that this polymer is more effective than a completely fluorinated sulfonic acid containing polymer. For such uses the sulfonic acid content need not be high, say only 1 to 20 mole percent, preferably about 2 to 10 mole percent of the  
30 repeat units in the polymer having sulfonic acid groups. The polymer may be crosslinked, in which case it may be soluble in the medium (for instance tetrahydrofuran), or it may be crosslinked so it swollen but not dissolved by the medium, Or it may be  
35 coated onto a substrate and optionally chemically attached and/or crosslinked, so it may easily be separated from the other process ingredients.

One of the monomers that may be polymerized by the above catalysts is ethylene (E), either by itself to form a homopolymer; or with  $\alpha$ -olefins and/or olefinic esters or carboxylic acids. The structure of the polymer may be unique in terms of several measurable properties.

These polymers, and others herein, can have unique structures in terms of the branching in the polymer. Branching may be determined by NMR spectroscopy (see the Examples for details), and this analysis can determine the total number of branches, and to some extent the length of the branches. Herein the amount of branching is expressed as the number of branches per 1000 of the total methylene ( $-\text{CH}_2-$ ) groups in the polymer, with one exception. Methylene groups that are in an ester grouping, i.e.  $-\text{CO}_2\text{R}$ , are not counted as part of the 1000 methylenes. These methylene groups include those in the main chain and in the branches. These polymers, which are E homopolymers, have a branch content of about 80 to about 150 branches per 1000 methylene groups, preferably about 100 to about 130 branches per 1000 methylene groups. These branches do not include polymer end groups. In addition the distribution of the sizes (lengths) of the branches is unique. Of the above total branches, for every 100 that are methyl, about 30 to about 90 are ethyl, about 4 to about 20 are propyl, about 15 to about 50 butyl, about 3 to about 15 are amyl, and about 30 to about 140 are hexyl or longer, and it is preferred that for every 100 that are methyl, about 50 to about 75 are ethyl, about 5 to about 15 are propyl, about 24 to about 40 are butyl, about 5 to 10 are amyl, and about 65 to about 120 are hexyl or larger. These E homopolymers are often amorphous, although in some there may be a small amount of crystallinity.

Another polyolefin, which is an E homopolymer that can be made by these catalysts has about 20 to about 150 branches per 1000 methylene groups, and, per 100

methy1 groups, about 4 to about 20 ethyl groups, about 1 to about 12 propyl groups, about 1 to about 12 butyl group, about 1 to about 10 amyl groups, and 0 to about 20 hexyl or larger groups. Preferably this polymer has  
5 about 40 to about 100 methy1 groups per 1000 methylene groups, and per 100 methy1 groups, about 6 to about 15 ethyl groups, about 2 to about 10 propyl groups, about 2 to about 10 butyl groups, about 2 to about 8 amyl groups, and about 2 to about 15 hexyl or larger groups.

10 Many of the polyolefins herein, including homopolyethylenes, may be crosslinked by various methods known in the art, for instance by the use of peroxide or other radical generating species which can crosslink these polymers. Such crosslinked polymers  
15 are novel when the uncrosslinked polymers from which they are derived are novel, because for the most part the structural feature(s) of the uncrosslinked polymers which make them novel will be carried over into the crosslinked forms.

20 In addition, some of the E homopolymers have an exceptionally low density, less than about 0.86 g/mL, preferably about 0.85 g/mL or less, measured at 25°C. This density is based on solid polymer.

Homopolymers of polypropylene (P) can also have  
25 unusual structures. Similar effects have been observed with other  $\alpha$ -olefins (e.g. 1-hexene). A "normal" P homopolymer will have one methy1 group for each methylene group (or 1000 methy1 groups per 1000 methylene groups), since the normal repeat unit is -  
30  $\text{CH}(\text{CH}_3)\text{CH}_2$ -. However, using a catalyst of formula (I) in which M is Ni(II) in combination with an alkyl aluminum compound it is possible to produce a P homopolymer with about 400 to about 600 methy1 groups per 1000 methylene groups, preferably about 450 to  
35 about 550 methy1 groups per 1000 methylene groups. Similar effects have been observed with other  $\alpha$ -olefins (e.g. 1-hexene).



In the polymerization processes described herein olefinic esters and/or carboxylic acids may also be present, and of course become part of the copolymer formed. These esters may be copolymerized with one or  
5 more of E and one or more  $\alpha$ -olefins. When copolymerized with E alone polymers with unique structures may be formed.

In many such E/olefinic ester and/or carboxylic acid copolymers the overall branching level and the  
10 distribution of branches of various sizes are unusual. In addition, where and how the esters or carboxylic acids occur in the polymer is also unusual. A relatively high proportion of the repeat units derived from the olefinic esters are at the ends of branches.  
15 In such copolymers, it is preferred that the repeat units derived from the olefinic esters and carboxylic acids are about 0.1 to 40 mole percent of the total repeat units, more preferably about 1 to about 20 mole percent. In a preferred ester, m is 0 and  $R^1$  is  
20 hydrocarbyl or substituted hydrocarbyl. It is preferred that  $R^1$  is alkyl containing 1 to 20 carbon atoms, more preferred that it contains 1 to 4 carbon atoms, and especially preferred that  $R^1$  is methyl.

One such preferred dipolymer has about 60 to 100  
25 methyl groups (excluding methyl groups which are esters) per 1000 methylene groups in the polymer, and contains, per 100 methyl branches, about 45 to about 65 ethyl branches, about 1 to about 3 propyl branches, about 3 to about 10 butyl branches, about 1 to about 3  
30 amyl branches, and about 15 to about 25 hexyl or longer branches. In addition, the ester and carboxylic acid containing repeat units are often distributed mostly at the ends of the branches as follows. If the branches, and the carbon atom to which they are attached to the  
35 main chain, are of the formula  $-\text{CH}(\text{CH}_2)_n\text{CO}_2\text{R}^1$ , wherein the CH is part of the main chain, then in some of these polymers about 40 to about 50 mole percent of ester groups are found in branches where n is 5 or more,

about 10 to about 20 mole percent when n is 4, about 20 to 30 mole percent when n is 1, 2 and 3 and about 5 to about 15 mole percent when n is 0. When n is 0, an acrylate ester has polymerized "normally" as part of the main chain, with the repeat unit  $-\text{CH}_2-\text{CHCO}_2\text{R}^1-$ .

These branched polymers which contain olefin and olefinic ester monomer units, particularly copolymers of ethylene and methyl acrylate and/or other acrylic esters are particularly useful as viscosity modifiers for lubricating oils, particularly automotive lubricating oils.

Under certain polymerization conditions, some of the polymerization catalysts described herein produce polymers whose structure is unusual, especially considering from what compounds (monomers) the polymers were made, and the fact that polymerization catalysts used herein are so-called transition metal coordination catalysts (more than one compound may be involved in the catalyst system, one of which must include a transition metal). Some of these polymers were described in a somewhat different way above, and they may be described as "polyolefins" even though they may contain other monomer units which are not olefins (e.g., olefinic esters). In the polymerization of an unsaturated compound of the formula  $\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_e\text{G}$ , wherein e is 0 or an integer of 1 or more, and G is hydrogen or  $-\text{CO}_2\text{R}^1$ , the usual ("normal") polymeric repeat unit obtained would be  $-\text{CH}_2-\text{CH}[(\text{CH}_2)_e\text{G}]$ -, wherein the branch has the formula  $-(\text{CH}_2)_e\text{G}$ . However, with some of the instant catalysts a polymeric unit may be  $-\text{CH}_2-\text{CH}[(\text{CH}_2)_f\text{G}]$ -, wherein  $f \neq e$ , and f is 0 or an integer of 1 or more. If  $f < e$ , the "extra" methylene groups may be part of the main polymer chain. If  $f > e$  (parts of) additional monomer molecules may be incorporated into that branch. In other words, the structure of any polymeric unit may be irregular and different for monomer molecules incorporated into the polymer, and the structure of such a polymeric unit obtained could

be rationalized as the result of "migration of the active polymerizing site" up and down the polymer chain, although this may not be the actual mechanism. This is highly unusual, particularly for  
 5 polymerizations employing transition metal coordination catalysts.

For "normal" polymerizations, wherein the polymeric unit  $-\text{CH}_2-\text{CH}[(\text{CH}_2)_e\text{G}] -$  is obtained, the theoretical amount of branching, as measured by the  
 10 number of branches per 1000 methylene ( $-\text{CH}_2-$ ) groups can be calculated as follows which defines terms "theoretical branches" or "theoretical branching" herein:

$$15 \quad \text{Theoretical branches} = \frac{1000 \times \text{Total mole fraction of } \alpha\text{-olefins}}{(\sum (2 \times \text{mole fraction } e=0)) + (\sum (\text{mole fraction } \alpha\text{-olefin} \times e))}$$

In this equation, an  $\alpha$ -olefin is any olefinic compound  $\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_e\text{G}$  wherein  $e \neq 0$ . Ethylene or an acrylic  
 20 compound are the cases wherein  $e=0$ . Thus to calculate the number of theoretical branches in a polymer made from 50 mole percent ethylene ( $e=0$ ), 30 mole percent propylene ( $e=1$ ) and 20 mole percent methyl 5-heptenoate ( $e=4$ ) would be as follows:

$$25 \quad \text{Theoretical branches} = \frac{1000 \times 0.5}{\{(2 \times 0.5)\} + \{(0.30 \times 1) + (0.20 \times 4)\}} = 238 \text{ (branches/1000 methylenes)}$$

The "1000 methylenes" include all of the methylene  
 30 groups in the polymer, including methylene groups in the branches.

For some of the polymerizations described herein, the actual amount of branching present in the polymer is considerably greater than or less than the above  
 35 theoretical branching calculations would indicate. For instance, when an ethylene homopolymer is made, there should be no branches, yet there are often many such branches. When an  $\alpha$ -olefin is polymerized, the

branching level may be much lower or higher than the theoretical branching level. It is preferred that the actual branching level is at 90% or less of the theoretical branching level, more preferably about 80% or less of the theoretical branching level, or 110% or more of the theoretical branching level, more preferably about 120% or more of the theoretical branching level. The polymer should also have at least about 50 branches per 1000 methylene units, preferably about 75 branches per 1000 methylene units, and more preferably about 100 branches per 1000 methylene units. In cases where there are "0" branches theoretically present, as in ethylene homopolymers or copolymers with acrylics, excess branches as a percentage cannot be calculated. In that instance if the polymer has 50 or more, preferably 75 or more branches per 1000 methylene groups, it has excess branches (i.e. in branches in which  $f > 0$ ).

These polymers also have "at least two branches of different lengths containing less than 6 carbon atoms each." By this is meant that branches of at least two different lengths (i.e. number of carbon atoms), and containing less than 6 carbon atoms, are present in the polymer. For instance the polymer may contain ethyl and butyl branches, or methyl and amyl branches.

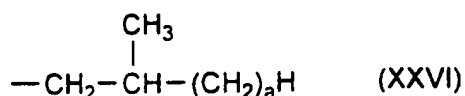
As will be understood from the above discussion, the lengths of the branches ("f") do not necessarily correspond to the original sizes of the monomers used ("e"). Indeed branch lengths are often present which do not correspond to the sizes of any of the monomers used and/or a branch length may be present "in excess". By "in excess" is meant there are more branches of a particular length present than there were monomers which corresponded to that branch length in the polymer. For instance, in the copolymerization of 75 mole percent ethylene and 25 mole percent 1-butene it would be expected that there would be 125 ethyl branches per 1000 methylene carbon atoms. If there

were more ethyl branches than that, they ~~would~~ be in excess compared to the theoretical branching. There may also be a deficit of specific length branches. If there were less than 125 ethyl branches per 1000 methylene groups in this polymer there would be a deficit. Preferred polymers have 90% or less or 110% or more of the theoretical amount of any branch length present in the polymer, and it is especially preferred if these branches are about 80% or less or about 120% or more of the theoretical amount of any branch length. In the case of the 75 mole percent ethylene/25 mole percent 1-butene polymer, the 90% would be about 113 ethyl branches or less, while the 110% would be about 138 ethyl branches or more. Such polymers may also or exclusively contain at least 50 branches per 1000 methylene atoms with lengths which should not theoretically (as described above) be present at all.

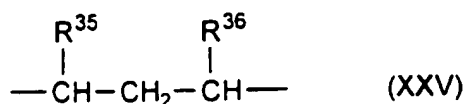
These polymers also have "at least two branches of different lengths containing less than 6 carbon atoms each." By this is meant that branches of at least two different lengths (i.e. number of carbon atoms), and containing less than 6 carbon atoms, are present in the polymer. For instance the polymer may contain ethyl and butyl branches, or methyl and amyl branches.

Some of the polymers produced herein are novel because of unusual structural features. Normally, in polymers of alpha-olefins of the formula  $\text{CH}_2=\text{CH}(\text{CH}_2)_a\text{H}$  wherein  $a$  is an integer of 2 or more made by coordination polymerization, the most abundant, and often the only, branches present in such polymers have the structure  $-(\text{CH}_2)_a\text{H}$ . Some of the polymers produced herein are novel because methyl branches comprise about 25% to about 75% of the total branches in the polymer. Such polymers are described in Examples 139, 162, 173 and 243-245. Some of the polymers produced herein are novel because in addition to having a high percentage (25-75%) of methyl branches (of the total branches present), they also contain linear branches of the

structure  $-(CH_2)_nH$  wherein  $n$  is an integer of six or greater. Such polymers are described in Examples 139, 173 and 243-245. Some of the polymers produced herein are novel because in addition to having a high  
 5 percentage (25-75%) of methyl branches (of the total branches present), they also contain the structure (XXVI), preferably in amounts greater than can be accounted for by end groups, and more preferably greater than 0.5 (XXVI) groups per thousand methyl  
 10 groups in the polymer greater than can be accounted for by end groups.



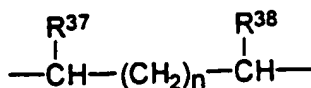
15 Normally, homo- and copolymers of one or more alpha-olefins of the formula  $CH_2=CH(CH_2)_aH$  wherein  $a$  is an integer of 2 or more contain as part of the polymer backbone the structure (XXV)



20 wherein  $R^{35}$  and  $R^{36}$  are alkyl groups. In most such polymers of alpha-olefins of this formula (especially those produced by coordination-type polymerizations), both of  $R^{35}$  and  $R^{36}$  are  $-(CH_2)_aH$ . However, in certain  
 25 of these polymers described herein, about 2 mole percent or more, preferably about 5 mole percent or more and more preferably about 50 mole percent or more of the total amount of (XXV) in said polymer consists  
 30 of the structure where one of  $R^{35}$  and  $R^{36}$  is a methyl group and the other is an alkyl group containing two or more carbon atoms. Furthermore, in certain of these polymers described herein, structure (XXV) may occur in side chains as well as in the polymer backbone.  
 35 Structure (XXV) can be detected by  $^{13}C$  NMR. The signal

for the carbon atom of the methylene group between the two methine carbons in (XXV) usually occurs in the  $^{13}\text{C}$  NMR at 41.9 to 44.0 ppm when one of  $\text{R}^{35}$  and  $\text{R}^{36}$  is a methyl group and the other is an alkyl group containing two or more carbon atoms, while when both  $\text{R}^{35}$  and  $\text{R}^{36}$  contain 2 or more carbon atoms, the signal for the methylene carbon atom occurs at 39.5 to 41.9 ppm. Integration provides the relative amounts of these structures present in the polymer. If there are interfering signals from other carbon atoms in these regions, they must be subtracted from the total integrals to give correct values for structure (XXV).

Normally, homo- and copolymers of one or more alpha-olefins of the formula  $\text{CH}_2=\text{CH}(\text{CH}_2)_a\text{H}$  wherein  $a$  is an integer of 2 or more (especially those made by coordination polymerization) contain as part of the polymer backbone structure (XXIV) wherein  $n$  is 0, 1, or 2. When  $n$  is 0, this structure is termed "head to head" polymerization. When  $n$  is 1, this structure is termed "head to tail" polymerization. When  $n$  is 2, this structure is termed "tail to tail" polymerization. In most such polymers of alpha-olefins of this formula (especially those produced by coordination-type polymerizations), both of  $\text{R}^{37}$  and  $\text{R}^{38}$  are  $-(\text{CH}_2)_a\text{H}$ . However some of the polymers of alpha-olefins of this formula described herein are novel in that they also contain structure (XXIV) wherein  $n = a$ ,  $\text{R}^{37}$  is a methyl group, and  $\text{R}^{38}$  is an alkyl group with 2 or more carbon atoms.

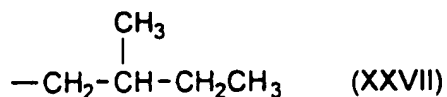


(XXV)

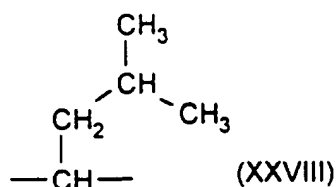
Normally polyethylene made by coordination polymerization has a linear backbone with either no

branching, or small amounts of linear branches. Some of the polyethylenes described herein are unusual in that they contain structure (XXVII) which has a methine carbon that is not part of the main polymer backbone.

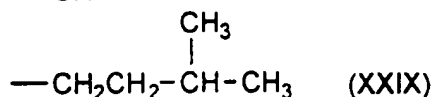
5



Normally, polypropylene made by coordination polymerization has methyl branches and few if any  
10 branches of other sizes. Some of the polypropylenes described herein are unusual in that they contain one or both of the structures (XXVIII) and (XXIX).



15

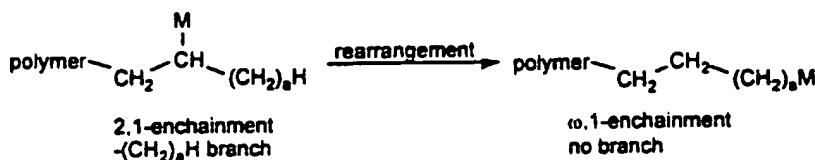


As the artisan understands, in coordination polymerization alpha-olefins of the formula  $\text{CH}_2=\text{CH}(\text{CH}_2)_a\text{H}$  may insert into the growing polymer chain  
20 in a 1,2 or 2,1 manner. Normally these insertion steps lead to 1,2- enchainment or 2,1-enchainment of the monomer. Both of these fundamental steps form a -  $(\text{CH}_2)_a\text{H}$  branch. However, with some catalysts herein, some of the initial product of 1,2 insertion can  
25 rearrange by migration of the coordinated metal atom to the end of the last inserted monomer before insertion of additional monomer occurs. This results in omega,2- enchainment and the formation of a methyl branch.





It is also known that with certain other catalysts, some of the initial product of 2,1 insertion can rearrange in a similar manner by migration of the coordinated metal atom to the end of the last inserted monomer. This results in omega,1-enchainment and no branch is formed.



Of the four types of alpha-olefin enchainment, omega,1-enchainment is unique in that it does not generate a branch. In a polymer made from an alpha-olefin of the formula  $\text{CH}_2=\text{CH}(\text{CH}_2)_a\text{H}$ , the total number of branches per 1000 methylene groups (B) can be expressed as:

$$B = (1000)(1-X_{\omega,1}) / [(1-X_{\omega,1})a + X_{\omega,1}(a+2)]$$

where  $X_{\omega,1}$  is the fraction of omega,1-enchainment

Solving this expression for  $X_{\omega,1}$  gives:

$$X_{\omega,1} = (1000 - aB) / (1000 + 2B)$$

This equation provides a means of calculating the fraction of omega,1-enchainment in a polymer of a linear alpha-olefin from the total branching B. Total branching can be measured by  $^1\text{H}$  NMR or  $^{13}\text{C}$  NMR. Similar equations can be written for branched alpha-

olefins. For example, the equation for 4-methyl-1-pentene is:

$$X_{\omega,1} = (2000 - 2B)/(1000 + 2B)$$

Most polymers of alpha-olefins made by other  
5 coordination polymerization methods have less than 5%  
omega,1-enchainment. Some of the alpha-olefin polymers  
described herein have unusually large amounts (say >5%)  
of omega,1-enchainment. In essence this is similar to  
stating that a polymer made from an  $\alpha$ -olefin has much  
10 less than the "expected" amount of branching. Although  
many of the polymerizations described herein give  
substantial amounts of  $\omega,1$ - and other unusual forms of  
enchainment of olefinic monomers, it has surprisingly  
been found that "unsymmetrical"  $\alpha$ -diimine ligands of  
15 formula (VIII) give especially high amounts of  $\omega,1$ -  
enchainment. In particular when  $R^2$  and  $R^5$  are phenyl,  
and one or both of these is substituted in such a way  
as different sized groups are present in the 2 and 6  
position of the phenyl ring(s),  $\omega,1$ -enchainment is  
20 enhanced. For instance, if one or both of  $R^2$  and  $R^5$   
are 2-t-butylphenyl, this enchainment is enhanced. In  
this context when  $R^2$  and/or  $R^5$  are "substituted" phenyl  
the substitution may be not only in the 2 and/or 6  
positions, but on any other position in the phenyl  
25 ring. For instance, 2,5-di-t-butylphenyl, and 2-t-  
butyl-4,6-dichlorophenyl would be included in  
substituted phenyl.

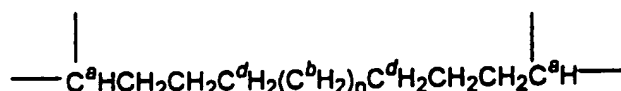
The steric effect of various groupings has been  
quantified by a parameter called  $E_s$ , see R. W. Taft,  
30 Jr., J. Am. Chem. Soc., vol. 74, p. 3120-3128, and M.S.  
Newman, Steric Effects in Organic Chemistry, John Wiley  
& Sons, New York, 1956, p. 598-603. For the purposes  
herein, the  $E_s$  values are those for o-substituted  
benzoates described in these publications. If the  
35 value for  $E_s$  for any particular group is not known, it  
can be determined by methods described in these  
publications. For the purposes herein, the value of  
hydrogen is defined to be the same as for methyl. It

is preferred that difference in  $E_s$ , when  $R^*$  and preferably also  $R^5$  is phenyl, between the groups substituted in the 2 and 6 positions of the phenyl ring is at least 0.15, more preferably at least about 0.20, and especially preferably about 0.6 or more. These phenyl groups may be unsubstituted or substituted in any other manner in the 3, 4 or 5 positions.

These differences in  $E_s$  are preferred in a diimine such as (VIII), and in any of the polymerization processes herein wherein a metal complex containing an  $\alpha$ -diimine ligand is used or formed. The synthesis and use of such  $\alpha$ -diimines is illustrated in Examples 454-463.

Because of the relatively large amounts of  $\omega,1$ -enchainment that may be obtained using some of the polymerization catalysts reported herein novel polymers can be made. Among these homopolypropylene (PP). In some of the PP's made herein the structure

20



(XXXX)

may be found. In this structure each  $C^a$  is a methine carbon atom that is a branch point, while each  $C^b$  is a methylene group that is more than 3 carbon atoms removed from any branch point ( $C^a$ ). Herein methylene groups of the type  $-C^bH_2-$  are termed  $\delta+$  (or delta+) methylene groups. Methylene groups of the type  $-C^dH_2-$ , which are exactly the third carbon atom from a branch point, are termed  $\gamma$  (gamma) methylene groups. The NMR signal for the  $\delta+$  methylene groups occurs at about 29.75 ppm, while the NMR signal for the  $\gamma$  methylene groups appears at about 30.15 ppm. Ratios of these types of methylene groups to each other and the total number of methylene groups in the PP is done by the usual NMR integration techniques.

It is preferred that PP's made herein have about 25 to about 300  $\delta^+$  methylene groups per 1000 methylene groups (total) in the PP.

It is also preferred that the ratio of  $\delta^+:\gamma$  methylene groups in the PP be 0.7 to about 2.0.

The above ratios involving  $\delta^+$  and  $\gamma$  methylene groups in PP are of course due to the fact that high relatively high  $\omega,1$  enchainment can be obtained. It is preferred that about 30 to 60 mole percent of the monomer units in PP be enchainment in an  $\omega,1$  fashion. Using the above equation, the percent  $\omega,1$  enchainment for polypropylene can be calculated as:

$$\% \omega,1 = (100)(1000-B)/(1000+2B)$$

wherein B is the total branching (number of methyl groups) per 1000 methylene groups in the polymer.

Homo- or copolymers of one or more linear  $\alpha$ -olefins containing 3 to 8 carbon atoms may also have  $\delta^+$  carbon atoms in them, preferably at least about 1 or more  $\delta^+$  carbon atoms per 1000 methylene groups.

The above polymerization processes can of course be used to make relatively random copolymers (except for certain CO copolymers) of various possible monomers. However, some of them can also be used to make block polymers. A block polymer is conventionally defined as a polymer comprising molecules in which there is a linear arrangement of blocks, a block being a portion of a polymer molecule which the monomeric units have at least one constitutional or configurational feature absent from adjacent portions (definition from H. Mark, et al., Ed., Encyclopedia of Polymer Science and Engineering, Vol. 2, John Wiley & Sons, New York, 1985, p. 324). Herein in a block copolymer, the constitutional difference is a difference in monomer units used to make that block, while in a block homopolymer the same monomer(s) are used but the repeat units making up different blocks are different structure and/or ratios of types of structures.

Since it is believed that many of the polymerization processes herein have characteristics that often resemble those of living polymerizations, making block polymers may be relatively easy. One method is to simply allow monomer(s) that are being polymerized to be depleted to a low level, and then adding different monomer(s) or the same combination of monomers in different ratios. This process may be repeated to obtain polymers with many blocks.

Lower temperatures, say about less than 0°C, preferably about -10° to about -30°, tends to enhance the livingness of the polymerizations. Under these conditions narrow molecular weight distribution polymers may be obtained (see Examples 367-369 and 371), and block copolymers may also be made (Example 370).

As pointed out above, certain polymerization conditions, such as pressure, affect the microstructure of many polymers. The microstructure in turn affects many polymer properties, such as crystallization. Thus, by changing polymerization conditions, such as the pressure, one can change the microstructure of the part of the polymer made under those conditions. This of course leads to a block polymer, a polymer have defined portions having structures different from other defined portions. This may be done with more than one monomer to obtain a block copolymer, or may be done with a single monomer or single mixture of monomers to obtain a block homopolymer. For instance, in the polymerization of ethylene, high pressure sometimes leads to crystalline polymers, while lower pressures give amorphous polymers. Changing the pressure repeatedly could lead to an ethylene homopolymer containing blocks of amorphous polyethylene and blocks of crystalline polyethylene. If the blocks were of the correct size, and there were enough of them, a thermoplastic elastomeric homopolyethylene could be

produced. Similar polymers could possibly be made from other monomer(s), such as propylene.

Homopolymers of  $\alpha$ -olefins such as propylene, that is polymers which were made from a monomer that  
5 consisted essentially of a single monomer such as propylene, which are made herein, sometimes exhibit unusual properties compared to their "normal" homopolymers. For instance, such a homopolypropylene usually would have about 1000 methyl groups per 1000  
10 methylene groups. Polypropylenes made herein typically have about half that many methyl groups, and in addition have some longer chain branches. Other  $\alpha$ -olefins often give polymers whose microstructure is analogous to these polypropylenes when the above  
15 catalysts are used for the polymerization.

These polypropylenes often exhibit exceptionally low glass transition temperatures (Tg's). "Normal" polypropylene has a Tg of about  $-17^{\circ}\text{C}$ , but the polypropylenes herein have a Tg of  $-30^{\circ}\text{C}$  or less,  
20 preferably about  $-35^{\circ}\text{C}$  or less, and more preferably about  $-40^{\circ}\text{C}$  or less. These Tg's are measured by Differential Scanning Calorimetry at a heating rate of  $10^{\circ}\text{C}/\text{min}$ , and the Tg is taken as the midpoint of the transition. These polypropylenes preferably have at  
25 least 50 branches (methyl groups) per 1000 carbon atoms, more preferably at least about 100 branches per 1000 methylene groups.

Previously, when cyclopentene was coordination polymerized to higher molecular weights, the resulting  
30 polymer was essentially intractable because of its very high melting point, greatly above  $300^{\circ}\text{C}$ . Using the catalysts here to homopolymerize cyclopentene results in a polymer that is tractable, i.e., may be reformed, as by melt forming. Such polymers have an end of  
35 melting point of about  $320^{\circ}\text{C}$  or less, preferably about  $300^{\circ}\text{C}$  or less, or a melting point of about  $275^{\circ}\text{C}$  or less, preferably about  $250^{\circ}\text{C}$  or less. The melting point is determined by Differential Scanning

Calorimetry at a heating rate of 15°C/min, and taking the maximum of the melting endotherm as the melting point. However these polymers tend to have relatively diffuse melting points, so it is preferred to measure the "melting point" by the end of melting point. The method is the same, except the end of melting is taken as the end (high temperature end) of the melting endotherm which is taken as the point at which the DSC signal returns to the original (extrapolated) baseline. Such polymers have an average degree of polymerization (average number of cyclopentene repeat units per polymer chain) of about 10 or more, preferably about 30 or more, and more preferably about 50 or more.

In these polymers, enchainment of the cyclopentene repeat units is usually as cis-1,3-pentylene units, in contrast to many prior art cyclopentenenes which were enchainned as 1,2-cyclopentylene units. It is preferred that about 90 mole percent or more, more preferably about 95 mole percent or more of the enchainned cyclopentene units be enchainned as 1,3-cyclopentylene units, which are preferably cis-1,3-cyclopentylene units.

The X-ray powder diffraction pattern of the instant poly(cyclopentenenes) is also unique. To produce cyclopentene polymer samples of uniform thickness for X-ray measurements, powder samples were compressed into disks approximately 1 mm thick and 32 mm in diameter. X-ray powder diffraction patterns of the samples were collected over the range 10-50° 2θ. The diffraction data were collected using an automated Philips θ-θ diffractometer (Philips X'pert System) operating in the symmetrical transmission mode (Ni-filtered CuKα radiation, equipped with a diffracted beam collimator (Philips Thin Film Collimator system), Xe filled proportional detector, fixed step mode (0.05°/step), 12.5 sec./step, 1/4° divergence slit). Reflection positions were identified using the peak finding routine in the APD suite of programs provided with the

X'pert System. The X-ray powder diffraction pattern had reflections at approximately  $17.3^\circ$ ,  $19.3^\circ$ ,  $24.2^\circ$ , and  $40.7^\circ$   $2\theta$ , which correspond to d-spacings of approximately 0.512, 0.460, 0.368 and 0.222 nm, respectively. These polymers have a monoclinic unit cell of the approximate dimensions:  $a=0.561$  nm;  $b=0.607$  nm;  $c=7.37$  nm; and  $\beta=123.2^\circ$ .

Copolymers of cyclopentene and various other olefins may also be made. For instance a copolymer of ethylene and cyclopentene may also be made. In such a copolymer it is preferred that at least 50 mole percent, more preferably at least about 70 mole percent, of the repeat units are derived from cyclopentene. As also noted above, many of the polymerization systems described herein produce polyethylenes that have considerable branching in them. Likewise the ethylene units which are copolymerized with the cyclopentene herein may also be branched, so it is preferred that there be at least 20 branches per 1000 methylene carbon atoms in such copolymers. In this instance, the "methylene carbon atoms" referred to in the previous sentence do not include methylene groups in the cyclopentene rings. Rather it includes methylene groups only derived from ethylene or other olefin, but not cyclopentene.

Another copolymer that may be prepared is one from cyclopentene and an  $\alpha$ -olefin, more preferably a linear  $\alpha$ -olefin. It is preferred in such copolymers that repeat units derived from cyclopentene are 50 mole percent or more of the repeat units. As mentioned above,  $\alpha$ -olefins may be enchainned in a 1, $\omega$  fashion, and it is preferred that at least 10 mole percent of the repeat units derived from the  $\alpha$ -olefin be enchainned in such a fashion. Ethylene may also be copolymerized with the cyclopentene and  $\alpha$ -olefin.

Poly(cyclopentene) and copolymers of cyclopentene, especially those that are (semi)crystalline, may be used as molding and extrusion resins. They may contain



various materials normally found in resins, such as fillers, reinforcing agents, antioxidants, antiozonants, pigments, tougheners, compatibilizers, dyes, flame retardant, and the like. These polymers  
5 may also be drawn or melt spun into fibers. Suitable tougheners and compatibilizers include polycyclopentene resin which has been grafted with maleic anhydride, an grafted EPDM rubber, a grafted EP rubber, a functionalized styrene/butadiene rubber, or other  
10 rubber which has been modified to selectively bond to components of the two phases.

In all of the above homo- and copolymers of cyclopentene, where appropriate, any of the preferred state may be combined any other preferred state(s).

15 The homo- and copolymers of cyclopentene described above may used or made into certain forms as described below:

1. The cyclopentene polymers described above may be part of a polymer blend. That is they may be  
20 mixed in any proportion with one or more other polymers which may be thermoplastics and/or elastomers. Suitable polymers for blends are listed below in the listing for blends of other polymers described herein. One preferred type of polymer which may be blended is a  
25 toughening agent or compatibilizer, which is often elastomeric and/or contains functional groups which may help compatibilize the mixture, such as epoxy or carboxyl.

2. The polycyclopentenenes described herein are  
30 useful in a nonwoven fabric comprising fibrillated three-dimensional network fibers prepared by using of a polycyclopentene resin as the principal component. It can be made by flash-spinning a homogeneous solution containing a polycyclopentene. The resultant nonwoven  
35 fabric is excellent in heat resistance, dimensional stability and solvent resistance.

3. A shaped part of any of the cyclopentene containing resins. This part may be formed by

injection molding, extrusion, and thermoforming. Exemplary uses include molded part for automotive use, medical treatment container, microwave-range container, food package container such as hot packing container, oven container, retort container, etc., and heat-resisting transparent container such as heat-resisting bottle.

4. A sheet or film of any of the cyclopentene containing resins. This sheet or film may be clear and may be used for optical purposes (i.e. breakage resistant glazing). The sheet or film may be oriented or unoriented. Orientation may be carried out by any of the known methods such a uniaxial or biaxial drawing. The sheet or film may be stampable or thermoformable.

5. The polycyclopentene resins are useful in nonwoven fabrics or microfibers which are produced by melt-blowing a material containing as a main component a polycyclopentene. A melt-blowing process for producing a fabric or fiber comprises supplying a polycyclopentene in a molten form from at least one orifice of a nozzle into a gas stream which attenuates the molten polymer into microfibers. The nonwoven fabrics are excellent in heat-resistant and chemical resistant characteristics, and are suitable for use as medical fabrics, industrial filters, battery separators and so forth. The microfibers are particularly useful in the field of high temperature filtration, coalescing and insulation.

6. A laminate in which one or more of the layers comprises a cyclopentene resin. The laminate may also contain adhesives, and other polymers in some or all of the layers, or other materials such as paper, metal foil, etc. Some or all of the layers, may be oriented in the same or different directions. The laminate as a whole may also be oriented. Such materials are useful for containers, or other uses where barrier properties are required.

7. A fiber of a cyclopentene polymer. This fiber may be undrawn or drawn to further orient it. It is useful for apparel and in industrial application where heat resistance and/or chemical resistance are important.

8. A foam or foamed object of a cyclopentene polymer. The foam may be formed in any conventional manner such as by using blowing agents.

9. The cyclopentene resins may be microporous membranes. They may be used in process wherein semi-permeable membranes are normally used.

In addition, the cyclopentene resins may be treated or mixed with other materials to improve certain properties, as follows:

1. They may further be irradiated with electron rays. This often improves heat resistance and/or chemical resistance, and is relatively inexpensive. Thus the molding is useful as a material required to have high heat resistance, such as a structural material, a food container material, a food wrapping material or an electric or electronic part material, particularly as an electric or electronic part material, because it is excellent in soldering resistance.

2. Parts with a crystallinity of at least 20% may be obtained by subjecting cyclopentene polymers having an end of melting point between 240 and 300°C to heat treatment (annealing) at a temperature of 120°C to just below the melting point of the polymer. Preferred conditions are a temperature of 150 to 280°C. for a period of time of 20 seconds to 90 minutes, preferably to give a cyclopentene polymer which has a heat deformation temperature of from 200 to 260°C. These parts have good physical properties such as heat resistance and chemical resistance, and thus are useful for, for example, general construction materials, electric or electronic devices, and car parts.

3. Cyclopentene resins may be nucleated to promote crystallization during processing. An example would be a polycyclopentene resin composition containing as main components (A) 100 parts by weight of a polycyclopentene and (B) 0.01 to 25 parts by weight of one or more nucleating agents selected from the group consisting of (1) metal salts of organic acids, (2) inorganic compounds, (3) organophosphorus compounds, and/or (4) metal salts of ionic hydrocarbon copolymer. Suitable nucleating agents may be sodium methylenebis(2,4-di-tertbutylphenyl) acid phosphate, sodium bis(4-tert-butylphenyl) phosphate, aluminum p-(tert-butyl) benzoate, talc, mica, or related species. These could be used in a process for producing polycyclopentene resin moldings by molding the above polycyclopentene resin composition at a temperature above their melting point.

4. Flame retardants and flame retardant combinations may be added to a cyclopentene polymer. Suitable flame retardants include a halogen-based or phosphorus-based flame retardant, antimony trioxide, antimony pentoxide, sodium antimonate, metallic antimony, antimony trichloride, antimony pentachloride, antimony trisulfide, antimony pentasulfide, zinc borate, barium metaborate or zirconium oxide. They may be used in conventional amounts.

5. Antioxidants may be used in conventional amounts to improve the stability of the cyclopentene polymers. For instance 0.005 to 30 parts by weight, per 100 parts by weight of the cyclopentene polymer, of an antioxidant selected from the group consisting of a phosphorous containing antioxidant, a phenolic antioxidant or a combination thereof. The phosphorous containing antioxidant may be a monophosphite or diphosphite or mixture thereof and the phenolic antioxidant may be a dialkyl phenol, trialkyl phenol, diphenylmonoalkoxyphenol, a tetraalkyl phenol, or a mixture thereof. A sulfur-containing antioxidant may

also be used alone or in combination with other antioxidants.

6. Various fillers or reinforcers, such as particulate or fibrous materials, may be added to  
5 improve various physical properties.

7. "Special" physical properties can be obtained by the use of specific types of materials. Electrically conductive materials such as fine metallic  
10 wires or graphite may be used to render the polymer electrically conductive. The temperature coefficient of expansion may be regulated by the use of appropriate fillers, and it may be possible to even obtain materials with positive coefficients of expansion. Such materials are particularly useful in electrical  
15 and electronic parts.

8. The polymer may be crosslinked by irradiation or chemically as by using peroxides, optionally in the presence of suitable coagents. Suitable peroxides include benzoyl peroxide, lauroyl  
20 peroxide, dicumyl peroxide, tert-butyl peroxide, tert-butylperoxybenzoate, tert-butylcumyl peroxide, tert-butylhydroperoxide, 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane, 2,5-dimethyl-2,5-di(tert-butylperoxy)hexyne-3,1,1-bis(tert-  
25 butylperoxyisopropyl)benzene, 1,1-bis(tert-butylperoxy)-3,3,5-trimethylcyclohexane, n-butyl-4,4-bis(tert-butylperoxy)valerate, 2,2-bis(tert-butylperoxy)butane and tert-butylperoxybenzene.

When polymerizing cyclopentene, it has been found  
30 that some of the impurities that may be found in cyclopentene poison or otherwise interfere with the polymerizations described herein. Compounds such as 1,3-pentadiene (which can be removed by passage through 5A molecular sieves), cyclopentadiene (which can be  
35 removed by distillation from Na), and methylenecyclobutane (which can be removed by distillation from polyphosphoric acid), may interfere

with the polymerization, and their level should be kept as low as practically possible.

The above polymers (in general) are useful in many applications. Crystalline high molecular weight  
5 polymers are useful as molding resins, and for films for use in packaging. Amorphous resins are useful as elastomers, and may be crosslinked by known methods, such as by using free radicals. When such amorphous resins contain repeat units derived from polar monomers  
10 they are oil resistant. Lower molecular weight polymers are useful as oils, such as in polymer processing aids. When they contain polar groups, particularly carboxyl groups, they are useful in adhesives.

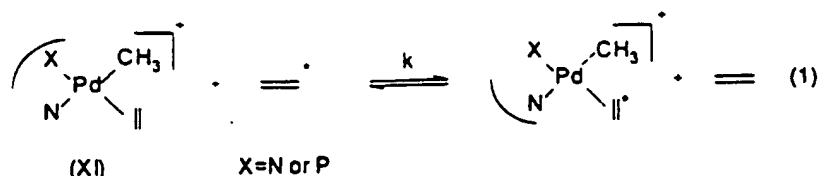
15 In many of the above polymerizations, the transition metal compounds employed as (part of the) catalysts contain(s) (a) metal atom(s) in a positive oxidation state. In addition, these complexes may have a square planar configuration about the metal, and the  
20 metal, particularly nickel or palladium, may have a  $d^8$  electronic configuration. Thus some of these catalysts may be said to have a metal atom which is cationic and has a  $d^8$ -square planar configuration.

In addition these catalysts may have a bidentate  
25 ligand wherein coordination to the transition metal is through two different nitrogen atoms or through a nitrogen atom and a phosphorus atom, these nitrogen and phosphorus atoms being part of the bidentate ligand. It is believed that some of these compounds herein are  
30 effective polymerization catalysts at least partly because the bidentate ligands have sufficient steric bulk on both sides of the coordination plane (of the square planar complex). Some of the Examples herein with the various catalysts of this type illustrate the  
35 degree of steric bulk which may be needed for such catalysts. If such a complex contains a bidentate ligand which has the appropriate steric bulk, it is

believed that it produces polyethylene with a degree of polymerization of at least about 10 or more.

It is also believed that the polymerization catalysts herein are effective because unpolymerized olefinic monomer can only slowly displace from the complex a coordinated olefin which may be formed by  $\beta$ -hydride elimination from the growing polymer chain which is attached to the transition metal. The displacement can occur by associative exchange.

Increasing the steric bulk of the ligand slows the rate of associative exchange and allows polymer chain growth. A quantitative measure of the steric bulk of the bidentate ligand can be obtained by measuring at  $-85^{\circ}\text{C}$  the rate of exchange of free ethylene with complexed ethylene in a complex of formula (XI) as shown in equation 1 using standard  $^1\text{H}$  NMR techniques, which is called herein the Ethylene Exchange Rate (EER). The neutral bidentate ligand is represented by YN where Y is either N or P. The EER is measured in this system. In this measurement system the metal is always Pd, the results being applicable to other metals as noted below. Herein it is preferred for catalysts to contain bidentate ligands for which the second order rate constant for Ethylene Exchange Rate is about  $20,000\text{ L}\cdot\text{mol}^{-1}\text{s}^{-1}$  or less when the metal used in the polymerization catalyst is palladium, more preferably about  $10,000\text{ L}\cdot\text{mol}^{-1}\text{s}^{-1}$  or less, and more preferably about  $5,000\text{ L}\cdot\text{mol}^{-1}\text{s}^{-1}$  or less. When the metal in the polymerization catalyst is nickel, the second order rate constant (for the ligand in EER measurement) is about  $50,000\text{ L}\cdot\text{mol}^{-1}\text{s}^{-1}$ , more preferably about  $25,000\text{ L}\cdot\text{mol}^{-1}\text{s}^{-1}$  or less, and especially preferably about  $10,000\text{ L}\cdot\text{mol}^{-1}\text{s}^{-1}$  or less. Herein the EER is measured using the compound (XI) in a procedure (including temperature) described in Examples 21-23.



In these polymerizations it is preferred if the bidentate ligand is an  $\alpha$ -diimine. It is also preferred if the olefin has the formula  $R^{17}CH=CH_2$ , wherein  $R^{17}$  is hydrogen or n-alkyl.

In general for the polymers described herein, blends may be prepared with other polymers, and such other polymers may be elastomers, thermoplastics or thermosets. By elastomers are generally meant polymers whose  $T_g$  (glass transition temperature) and  $T_m$  (melting point), if present, are below ambient temperature, usually considered to be about  $20^\circ\text{C}$ . Thermoplastics are those polymers whose  $T_g$  and/or  $T_m$  are at or above ambient temperature. Blends can be made by any of the common techniques known to the artisan, such as solution blending, or melt blending in a suitable apparatus such as a single or twin-screw extruder. Specific uses for the polymers of this application in the blends or as blends are listed below.

Blends may be made with almost any kind of elastomer, such as EP, EPDM, SBR, natural rubber, polyisoprene, polybutadiene, neoprene, butyl rubber, styrene-butadiene block copolymers, segmented polyester-polyether copolymers, elastomeric polyurethanes, chlorinated or chlorosulfonated polyethylene, (per)fluorinated elastomers such as copolymers of vinylidene fluoride, hexafluoropropylene and optionally tetrafluoroethylene, copolymers of tetrafluoroethylene and perfluoro(methyl vinyl ether), and copolymers of tetrafluoroethylene and propylene.

Suitable thermoplastics which are useful for blending with the polymers described herein include: polyesters such as poly(ethylene terephthalate), poly(butylene terephthalate), and poly(ethylene



adipate); polyamides such as nylon-6, nylon-6,6, nylon-12, nylon-12,12, nylon-11, and a copolymer of hexamethylene diamine, adipic acid and terephthalic acid; fluorinated polymers such as copolymers of ethylene and vinylidene fluoride, copolymers of tetrafluoroethylene and hexafluoropropylene, copolymers of tetrafluoroethylene and a perfluoro(alkyl vinyl ether) such as perfluoro(propyl vinyl ether), and poly(vinyl fluoride); other halogenated polymers such as poly(vinyl chloride) and poly(vinylidene chloride) and its copolymers; polyolefins such as polyethylene, polypropylene and polystyrene, and copolymers thereof; (meth)acrylic polymers such as poly(methyl methacrylate) and copolymers thereof; copolymers of olefins such as ethylene with various (meth) acrylic monomers such as alkyl acrylates, (meth)acrylic acid and ionomers thereof, and glycidyl (meth)acrylate); aromatic polyesters such as the copolymer of Bisphenol A and terephthalic and/or isophthalic acid; and liquid crystalline polymers such as aromatic polyesters or aromatic poly(ester-amides).

Suitable thermosets for blending with the polymers described herein include epoxy resins, phenol-formaldehyde resins, melamine resins, and unsaturated polyester resins (sometimes called thermoset polyesters). Blending with thermoset polymers will often be done before the thermoset is crosslinked, using standard techniques.

The polymers described herein may also be blended with uncrosslinked polymers which are not usually considered thermoplastics for various reasons, for instance their viscosity is too high and/or their melting point is so high the polymer decomposes below the melting temperature. Such polymers include poly(tetrafluoroethylene), aramids such as poly(p-phenylene terephthalate) and poly(m-phenylene isophthalate), liquid crystalline polymer such as

poly(benzoxazoles), and non-melt processible polyimides which are often aromatic polyimides.

All of the polymers disclosed herein may be mixed with various additives normally added to elastomers and thermoplastics [see EPSE (below), vol. 14, p. 327-410]. For instance reinforcing, non-reinforcing and conductive fillers, such as carbon black, glass fiber, minerals such as clay, mica and talc, glass spheres, barium sulfate, zinc oxide, carbon fiber, and aramid fiber or fibrids, may be used. Antioxidants, antiozonants, pigments, dyes, delusterants, compounds to promote crosslinking may be added. Plasticizers such as various hydrocarbon oils may also be used.

The following listing is of some uses for polyolefins, which are made from linear olefins and do not include polar monomers such as acrylates, which are disclosed herein. In some cases a reference is given which discusses such uses for polymers in general. All of these references are hereby included by reference. For the references, "U" refers to W. Gerhartz, et al., Ed., Ullmann's Encyclopedia of Industrial Chemistry, 5th Ed. VCH Verlagsgesellschaft mbH, Weinheim, for which the volume and page number are given, "ECT3" refers to the H. F. Mark, et al., Ed., Kirk-Othmer Encyclopedia of Chemical Technology, 4th Ed., John Wiley & Sons, New York, "ECT4" refers to the J. I. Kroschwitz, et al., Ed., Kirk-Othmer Encyclopedia of Chemical Technology, 4th Ed., John Wiley & Sons, New York, for which the volume and page number are given, "EPST" refers to H. F. Mark, et al., Ed., Encyclopedia of Polymer Science and Technology, 1st Ed., John Wiley & Sons, New York, for which the volume and page number are given, "EPSE" refers to H. F. Mark, et al., Ed., Encyclopedia of Polymer Science and Engineering, 2nd Ed., John Wiley & Sons, New York, for which volume and page numbers are given, and "PM" refers to J. A. Brydson, ed., Plastics Materials, 5 Ed., Butterworth-Heinemann, Oxford, UK, 1989, and the page is given. In

these uses, a polyethylene, polypropylene and a copolymer of ethylene and propylene are preferred.

1. Tackifiers for low strength adhesives (U, vol. A1, p. 235-236) are a use for these polymers.

5 Elastomeric and/or relatively low molecular weight polymers are preferred.

2. An oil additive for smoke suppression in single-stroke gasoline engines is another use.

Elastomeric polymers are preferred.

10 3. The polymers are useful as base resins for hot melt adhesives (U, vol. A1, p. 233-234), pressure sensitive adhesives (U, vol. A1, p. 235-236) or solvent applied adhesives. Thermoplastics are preferred for hot melt adhesives. The polymers may also be used in a  
15 carpet installation adhesive.

4. Lubricating oil additives as Viscosity Index Improvers for multigrade engine oil (ECT3, Vol 14, p. 495-496) are another use. Branched polymers are preferred. Ethylene copolymer with acrylates or other  
20 polar monomers will also function as Viscosity Index Improvers for multigrade engine oil with the additional advantage of providing some dispersancy. 5. Polymer for coatings and/or penetrants for the protection of various porous items such as lumber and masonry,  
25 particularly out-of-doors. The polymer may be in a suspension or emulsion, or may be dissolved in a solvent.

6. Base polymer for caulking of various kinds is another use. An elastomer is preferred. Lower  
30 molecular weight polymers are often used.

7. The polymers may be grafted with various compounds particularly those that result in functional groups such as epoxy, carboxylic anhydride (for instance as with a free radically polymerized reaction  
35 with maleic anhydride) or carboxylic acid (EPSE, vol. 12, p. 445). Such functionalized polymers are particularly useful as tougheners for various thermoplastics and thermosets when blended. When the

polymers are elastomers, the functional groups which are grafted onto them may be used as curesites to crosslink the polymers. Maleic anhydride-grafted randomly-branched polyolefins are useful as tougheners  
5 for a wide range of materials (nylon, PPO, PPO/styrene alloys, PET, PBT, POM, etc.); as tie layers in multilayer constructs such as packaging barrier films; as hot melt, moisture-curable, and coextrudable adhesives; or as polymeric plasticizers. The maleic  
10 andhydride-grafted materials may be post reacted with, for example; amines, to form other functional materials. Reaction with aminopropyl trimethoxysilane would allow for moisture-curable materials. Reactions with di- and tri-amines would allow for viscosity  
15 modifications.

8. The polymers, particularly elastomers, may be used for modifying asphalt, to improve the physical properties of the asphalt and/or extend the life of asphalt paving.

20 9. The polymers may be used as base resins for chlorination or chlorosulfonation for making the corresponding chlorinated or chlorosulfonated elastomers. The unchlorinated polymers need not be elastomers themselves.

25 10. Wire insulation and jacketing may be made from any of the polyolefins (see EPSE, vol. 17, p. 828-842). In the case of elastomers it may be preferable to crosslink the polymer after the insulation or jacketing is formed, for example by free radicals.

30 11. The polymers, particularly the elastomers, may be used as tougheners for other polyolefins such as polypropylene and polyethylene.

12. The base for synthetic lubricants (motor oils) may be the highly branched polyolefins described  
35 herein (ECT3, vol. 14, p. 496-501).

13. The branched polyolefins herein can be used as drip suppressants when added to other polymers.

14. The branched polyolefins herein are especially useful in blown film applications because of their particular rheological properties (EPSE, vol. 7, p. 88-106). It is preferred that these polymers have  
5 some crystallinity.

15. The polymer described herein can be used to blend with wax for candles, where they would provide smoke suppression and/or drip control.

16. The polymers, especially the branched  
10 polymers, are useful as base resins for carpet backing, especially for automobile carpeting.

17. The polymers, especially those which are relatively flexible, are useful as capliner resins for carbonated and noncarbonated beverages.

18. The polymers, especially those having a  
15 relatively low melting point, are useful as thermal transfer imaging resins (for instance for imaging tee-shirts or signs).

19. The polymers may be used for extrusion or  
20 coextrusion coatings onto plastics, metals, textiles or paper webs.

20. The polymers may be used as a laminating adhesive for glass.

21. The polymers are useful as for blown or  
25 cast films or as sheet (see EPSE, vol. 7 p. 88-106; ECT4, vol. 11, p. 843-856; PM, p. 252 and p. 432ff). The films may be single layer or multilayer, the multilayer films may include other polymers, adhesives, etc. For packaging the films may be stretch-wrap,  
30 shrink-wrap or cling wrap. The films are useful form many applications such as packaging foods, geomembranes and pond liners. It is preferred that these polymers have some crystallinity.

22. The polymers may be used to form flexible  
35 or rigid foamed objects, such as cores for various sports items such as surf boards and liners for protective headgear. Structural foams may also be made. It is preferred that the polymers have some

crystallinity. The polymer of the foams may be crosslinked.

23. In powdered form the polymers may be used to coat objects by using plasma, flame spray or  
5 fluidized bed techniques.

24. Extruded films may be formed from these polymers, and these films may be treated, for example drawn. Such extruded films are useful for packaging of various sorts.

10 25. The polymers, especially those that are elastomeric, may be used in various types of hoses, such as automotive heater hose.

26. The polymers, especially those that are branched, are useful as pour point depressants for  
15 fuels and oils.

27. These polymers may be flash spun to nonwoven fabrics, particularly if they are crystalline (see EPSE vol. 10, p. 202-253) They may also be used to form spunbonded polyolefins (EPSE, vol. 6, p. 756-  
20 760). These fabrics are suitable as house wrap and geotextiles.

28. The highly branched, low viscosity polyolefins would be good as base resins for master-batching of pigments, fillers, flame-retardants, and  
25 related additives for polyolefins. 29. The polymers may be grafted with a compound containing ethylenic unsaturation and a functional group such as a carboxyl group or a derivative of a carboxyl group, such as ester, carboxylic anhydride or carboxylate salt. A  
30 minimum grafting level of about 0.01 weight percent of grafting agent based on the weight of the grafted polymer is preferred. The grafted polymers are useful as compatibilizers and/or tougheners. Suitable  
grafting agents include maleic, acrylic, methacrylic,  
35 itaconic, crotonic, alpha-methyl crotonic and cinnamic acids, anhydrides, esters and their metal salts and fumaric acid and their esters, anhydrides (when appropriate) and metal salts.

Copolymers of linear olefins with 4-vinylcyclohexene and other dienes may generally be used for all of the applications for which the linear olefins polymers (listed above) may be used. In addition they may be sulfur cured, so they generally can be used for any use for which EPDM polymers are used, assuming the olefin/4-vinylcyclohexene polymer is elastomeric.

Also described herein are novel copolymers of linear olefins with various polar monomers such as acrylic acid and acrylic esters. Uses for these polymers are given below. Abbreviations for references describing these uses in general with polymers are the same as listed above for polymers made from linear olefins.

1. Tackifiers for low strength adhesives (U, vol. A1, p. 235-236) are a use for these polymers. Elastomeric and/or relatively low molecular weight polymers are preferred.

2. The polymers are useful as base resins for hot melt adhesives (U, vol. A1, p. 233-234), pressure sensitive adhesives (U, vol. A1, p. 235-236) or solvent applied adhesives. Thermoplastics are preferred for hot melt adhesives. The polymers may also be used in a carpet installation adhesive.

3. Base polymer for caulking of various kinds is another use. An elastomer is preferred. Lower molecular weight polymers are often used.

4. The polymers, particularly elastomers, may be used for modifying asphalt, to improve the physical properties of the asphalt and/or extend the life of asphalt paving, see U.S. patent 3,980,598.

5. Wire insulation and jacketing may be made from any of the polymers (see EPSE, vol. 17, p. 828-842). In the case of elastomers it may be preferable to crosslink the polymer after the insulation or jacketing is formed, for example by free radicals.

6. The polymers, especially the branched polymers, are useful as base resins for carpet backing, especially for automobile carpeting.

7. The polymers may be used for extrusion or  
5 coextrusion coatings onto plastics, metals, textiles or paper webs.

8. The polymers may be used as a laminating adhesive for glass.

9. The polymers are useful as for blown or cast  
10 films or as sheet (see EPSE, vol. 7 p. 88-106; ECT4, vol. 11, p. 843-856; PM, p. 252 and p. 432ff). The films may be single layer or multilayer, the multilayer films may include other polymers, adhesives, etc. For  
15 packaging the films may be stretch-wrap, shrink-wrap or cling wrap. The films are useful for many  
applications such as packaging foods, geomembranes and pond liners. It is preferred that these polymers have some crystallinity.

10. The polymers may be used to form flexible  
20 or rigid foamed objects, such as cores for various sports items such as surf boards and liners for protective headgear. Structural foams may also be made. It is preferred that the polymers have some crystallinity. The polymer of the foams may be  
25 crosslinked.

11. In powdered form the polymers may be used to coat objects by using plasma, flame spray or fluidized bed techniques.

12. Extruded films may be formed from these  
30 polymers, and these films may be treated, for example drawn. Such extruded films are useful for packaging of various sorts.

13. The polymers, especially those that are elastomeric, may be used in various types of hoses,  
35 such as automotive heater hose.

14. The polymers may be used as reactive diluents in automotive finishes, and for this purpose



it is preferred that they have a relatively low molecular weight and/or have some crystallinity.

15        15. The polymers can be converted to ionomers, which when they possess crystallinity can be used as molding resins. Exemplary uses for these ionomeric molding resins are golf ball covers, perfume caps, sporting goods, film packaging applications, as tougheners in other polymers, and usually extruded detonator cords.

10        16. The functional groups on the polymers can be used to initiate the polymerization of other types of monomers or to copolymerize with other types of monomers. If the polymers are elastomeric, they can act as toughening agents.

15        17. The polymers can act as compatibilizing agents between various other polymers.

18. The polymers can act as tougheners for various other polymers, such as thermoplastics and thermosets, particularly if the olefin/polar monomer polymers are elastomeric.

20        19. The polymers may act as internal plasticizers for other polymers in blends. A polymer which may be plasticized is poly(vinyl chloride).

25        20. The polymers can serve as adhesives between other polymers.

30        21. With the appropriate functional groups, the polymers may serve as curing agents for other polymers with complimentary functional groups (i.e., the functional groups of the two polymers react with each other).

22. The polymers, especially those that are branched, are useful as pour point depressants for fuels and oils.

35        23. Lubricating oil additives as Viscosity Index Improvers for multigrade engine oil (ECT3, Vol 14, p. 495-496) are another use. Branched polymers are preferred. Ethylene copolymer with acrylates or other polar monomers will also function as Viscosity Index

Improvers for multigrade engine oil with the additional advantage of providing some dispersancy.

24. The polymers may be used for roofing  
5 membranes.

25. The polymers may be used as additives to various molding resins such as the so-called thermoplastic olefins to improve paint adhesion, as in automotive uses.

10 Polymers with or without polar monomers present are useful in the following uses. Preferred polymers with or without polar monomers are those listed above in the uses for each "type".

1. A flexible pouch made from a single layer or  
15 multilayer film (as described above) which may be used for packaging various liquid products such as milk, or powder such as hot chocolate mix. The pouch may be heat sealed. It may also have a barrier layer, such as a metal foil layer.

2. A wrap packaging film having differential  
20 cling is provided by a film laminate, comprising at least two layers; an outer reverse which is a polymer (or a blend thereof) described herein, which contains a tackifier in sufficient amount to impart cling  
25 properties; and an outer obverse which has a density of at least about 0.916 g/mL which has little or no cling, provided that a density of the outer reverse layer is at least 0.008 g/mL less than that of the density of the outer obverse layer. It is preferred that the  
30 outer obverse layer is linear low density polyethylene, and the polymer of the outer obverse layer have a density of less than 0.90 g/mL. All densities are measured at 25°C.

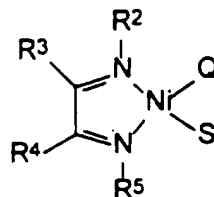
3. Fine denier fibers and/or multifilaments.  
35 These may be melt spun. They may be in the form of a filament bundle, a non-woven web, a woven fabric, a knitted fabric or staple fiber.

4. A composition comprising a mixture of the polymers herein and an antifogging agent. This composition is especially useful in film or sheet form because of its antifogging properties.

5        5. Elastic, randomly-branched olefin polymers are disclosed which have very good processability, including processing indices (PI's) less than or equal to 70 percent of those of a comparative linear olefin polymer and a critical shear rate at onset of surface  
10 melt fracture of at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a traditional linear olefin polymer at about the same I2 and Mw/Mn. The novel polymers may have higher low/zero shear viscosity and lower high  
15 shear viscosity than comparative linear olefin polymers made by other means. These polymers may be characterized as having: a) a melt flow ratio,  $I_{10}/I_2$ ,  $\geq 5.63$ , b) a molecular weight distribution, Mw/Mn, defined by the equation:  $Mw/Mn \leq (I_{10}/I_2) - 4.63$ , and c)  
20 a critical shear rate at onset of surface melt fracture of at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear olefin polymer having about the same I2 and Mw/Mn. Some blends of these polymer are characterized as  
25 having: a) a melt flow ratio,  $I_{10}/I_2$ ,  $\geq 5.63$ , b) a molecular weight distribution, Mw/Mn, defined by the equation:  $Mw/Mn \leq (I_{10}/I_2) - 4.63$ , and c) a critical shear rate at onset of surface melt fracture of at least 50 percent greater than the critical shear rate  
30 at the onset of surface melt fracture of a linear olefin polymer having about the same I2 and Mw/Mn and (b) at least one other natural or synthetic polymer chosen from the polymer of claims 1, 3, 4, 6, 332, or 343, a conventional high density polyethylene, low  
35 density polyethylene or linear low density polyethylene polymer. The polymers may be further characterized as having a melt flow ratio,  $I_{10}/I_2$ ,  $\geq 5.63$ , a molecular weight distribution, Mw/Mn, defined by the equation:

Mw/Mn  $\leq$  (I10/I2)-4.63, and a critical shear stress at onset of gross melt fracture of greater than about 400 kPa ( $4 \times 10^6$  dyne/cm<sup>2</sup>) and their method of manufacture are disclosed. The randomly-branched olefin polymers preferably have a molecular weight distribution from about 1.5 to about 2.5. The polymers described herein often have improved processability over conventional olefin polymers and are useful in producing fabricated articles such as fibers, films, and molded parts. For this paragraph, the value I2 is measured in accordance with ASTM D-1238-190/2.16 and I10 is measured in accordance with ASTM D-1238-190/10; critical shear rate at onset of surface melt fracture and processing index (PI) are defined in U.S. Patent 5,278,272, which is hereby included by reference.

In another process described herein, the product of the process described herein is an  $\alpha$ -olefin. It is preferred that in the process a linear  $\alpha$ -olefin is produced. It is also preferred that the  $\alpha$ -olefin contain 4 to 32, preferably 8 to 20, carbon atoms.



(XXXI)

When (XXXI) is used as a catalyst, a neutral Lewis acid or a cationic Lewis or Bronsted acid whose counterion is a weakly coordinating anion is also present as part of the catalyst system (sometimes called a "first compound" in the claims). By a "neutral Lewis acid" is meant a compound which is a Lewis acid capable for abstracting X' from (I) to form a weakly coordinating anion. The neutral Lewis acid is originally uncharged (i.e., not ionic). Suitable neutral Lewis acids include SbF<sub>5</sub>, Ar<sub>3</sub>B (wherein Ar is

aryl), and  $\text{BF}_3$ . By a cationic Lewis acid is meant a cation with a positive charge such as  $\text{Ag}^+$ ,  $\text{H}^+$ , and  $\text{Na}^+$ .

A preferred neutral Lewis acid is an alkyl aluminum compound, such as  $\text{R}^9\text{Al}$ ,  $\text{R}^9_2\text{AlCl}$ ,  $\text{R}^9_3\text{AlCl}_2$ , and  
5 " $\text{R}^9\text{AlO}$ " (alkylaluminosiloxane), wherein  $\text{R}^9$  is alkyl containing 1 to 25 carbon atoms, preferably 1 to 4 carbon atoms. Suitable alkyl aluminum compounds include methylaluminosiloxane,  $(\text{C}_2\text{H}_5)_2\text{AlCl}$ ,  $\text{C}_2\text{H}_5\text{AlCl}_2$ , and  
10  $[(\text{CH}_3)_2\text{CHCH}_2]_n\text{Al}$ .

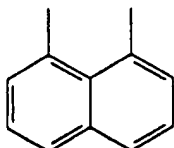
Relatively noncoordinating anions are known in the art, and the coordinating ability of such anions is known and has been discussed in the literature, see for instance W. Beck., et al., Chem. Rev., vol. 88 p. 1405-1421 (1988), and S. H. Strauss, Chem. Rev., vol. 93, p.  
15 927-942 (1993), both of which are hereby included by reference. Among such anions are those formed from the aluminum compounds in the immediately preceding paragraph and  $\text{X}^-$ , including  $\text{R}^9_3\text{AlX}^-$ ,  $\text{R}^9_2\text{AlClX}^-$ ,  $\text{R}^9_3\text{AlCl}_2\text{X}^-$ , and " $\text{R}^9\text{AlOX}^-$ ". Other useful noncoordinating anions  
20 include  $\text{BAF}^-$  {BAF = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate},  $\text{SbF}_6^-$ ,  $\text{PF}_6^-$ , and  $\text{BF}_4^-$ , trifluoromethanesulfonate, p-toluenesulfonate,  $(\text{R}_f\text{SO}_2)_2\text{N}^-$ , and  $(\text{C}_6\text{F}_5)_4\text{B}^-$ .

The temperature at which the process is carried  
25 out is about  $-100^\circ\text{C}$  to about  $+200^\circ\text{C}$ , preferably about  $0^\circ\text{C}$  to about  $150^\circ\text{C}$ , more preferably about  $25^\circ\text{C}$  to about  $100^\circ\text{C}$ . It is believed that at higher temperatures, lower molecular weight  $\alpha$ -olefins are produced, all other factors being equal. The pressure at which the  
30 polymerization is carried out is not critical, atmospheric pressure to about 275 MPa being a suitable range. It is also believed that increasing the pressure increases the relative amount of  $\alpha$ -olefin (as opposed to internal olefin) produced.

35 The process to make  $\alpha$ -olefins may be run in a solvent (liquid), and that is preferred. The solvent may in fact be the  $\alpha$ -olefin produced. Such a process may be started by using a deliberately added solvent

which is gradually displaced as the reaction proceeds. By solvent it is not necessarily meant that any or all of the starting materials and/or products are soluble in the (liquid) solvent.

- 5 In (I) it is preferred that  $R^3$  and  $R^4$  are both hydrogen or methyl or  $R^3$  and  $R^4$  taken together are



(An)

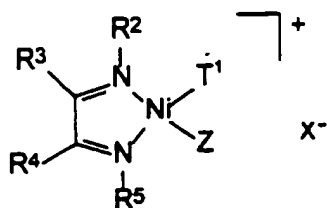
- 10 It is also preferred that each of Q and S is independently chlorine or bromine, and it is more preferred that both of Q and S in (XXXI) are chlorine or bromine.

- In (XXXI)  $R^2$  and  $R^5$  are hydrocarbyl or substituted hydrocarbyl. What these groups are greatly determines whether the  $\alpha$ -olefins of this process are made, or whether higher polymeric materials, i.e., materials containing over 25 ethylene units, are coproduced or produced almost exclusively. If  $R^2$  and  $R^5$  are highly sterically hindered about the nickel atom, the tendency is to produce higher polymeric material. For instance, when  $R^2$  and  $R^5$  are both 2,6-diisopropylphenyl mostly higher polymeric material is produced. However, when  $R^2$  and  $R^5$  are both phenyl, mostly the  $\alpha$ -olefins of this process are produced. Of course this will also be influenced by other reaction conditions such as temperature and pressure, as noted above. Useful groups for  $R^2$  and  $R^5$  are phenyl, and p-methylphenyl.

- As is understood by the artisan, in oligomerization reactions of ethylene to produce  $\alpha$ -olefins, usually a mixture of such  $\alpha$ -olefins is obtained containing a series of such  $\alpha$ -olefins differing from one another by two carbon atoms (an ethylene unit). The process for preparing  $\alpha$ -olefins described herein produces products with a high

percentage of terminal olefinic groups (as opposed to internal olefinic groups). The product mixture also contains a relatively high percentage of molecules which are linear. Finally relatively high catalyst efficiencies can be obtained.

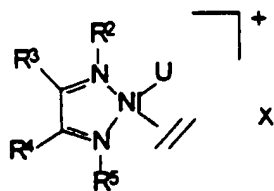
The  $\alpha$ -olefins described as being made herein may also be made by contacting ethylene with one of the compounds



10

(III)

or



(XXXIV)

15

wherein  $R^2$ ,  $R^3$ ,  $R^4$ , and  $R^5$  are as defined (and preferred) as described above (for the preparation of  $\alpha$ -olefins), and  $T^1$  is hydrogen or n-alkyl containing up to 38 carbon atoms, Z is a neutral Lewis base wherein the donating atom is nitrogen, sulfur, or oxygen, provided that if the donating atom is nitrogen then the pKa of the conjugate acid of that compound (measured in water) is less than about 6, U is n-alkyl containing up to 38 carbon atoms, and X is a noncoordinating anion (see above). The process conditions for making  $\alpha$ -olefins using (III) or (XXXIV) are the same as for using (XXXI) to make these compounds except a Lewis or Bronsted acid need not be present. Note that the double line in (XXXIV) represents a coordinated

20

25

ethylene molecule. (XXXIV) may be made from (II) by reaction of (III) with ethylene. In other words, (XXXIV) may be considered an active intermediate in the formation of  $\alpha$ -olefin from (III). Suitable groups for  
5 Z include dialkyl ethers such as diethyl ether, and alkyl nitriles such as acetonitrile.

In general,  $\alpha$ -olefins can be made by this process using as a catalyst a Ni[II] complex of an  $\alpha$ -diimine of formula (VIII), wherein the Ni[II] complex is made by  
10 any of the methods which are described above, using Ni[0], Ni[I] or Ni[II] precursors. All of the process conditions, and preferred groups on (VIII), are the same as described above in the process for making  $\alpha$ -olefins.

15

#### EXAMPLES

In the Examples, the following convention is used for naming  $\alpha$ -diimine complexes of metals, and the  $\alpha$ -diimine itself. The  $\alpha$ -diimine is indicated by the  
20 letters "DAB". To the left of the "DAB" are the two groups attached to the nitrogen atoms, herein usually called  $R^2$  and  $R^5$ . To the right of the "DAB" are the groups on the two carbon atoms of the  $\alpha$ -diimine group, herein usually termed  $R^3$  and  $R^4$ . To the right of all  
25 this appears the metal, ligands attached to the metal (such as Q, S and T), and finally any anions (X), which when "free" anions are designated by a superscript minus sign (i.e.,  $X^-$ ). Of course if there is a "free" anion present, the metal containing moiety is cationic.  
30 Abbreviations for these groups are as described in the Specification in the Note after Table 1. Analogous abbreviations are used for  $\alpha$ -diimines, etc.

In the Examples, the following abbreviations are used:

35  $\Delta H_f$  - heat of fusion  
acac - acetylacetonate  
Bu - butyl  
t-BuA - t-butyl acrylate



DMA - Dynamic Mechanical Analysis  
DME - 1,2-dimethoxyethane  
DSC - Differential Scanning Calorimetry  
E - ethylene  
5 EOC - end of chain  
Et - ethyl  
FC-75 - perfluoro(n-butyltetrahydrofuran)  
FOA - fluorinated octyl acrylate  
GPC - gel permeation chromatography  
10 MA - methyl acrylate  
MAO - methylaluminoxane  
Me - methyl  
MeOH - methanol  
MMAO - a modified methylaluminoxane in which  
15 about 25 mole percent of the methyl groups have been  
replaced by isobutyl groups  
M-MAO - see MMAO  
MMAO-3A - see MMAO  
Mn - number average molecular weight  
20 MVK - methyl vinyl ketone  
Mw- weight average molecular weight  
Mz - viscosity average molecular weight  
PD or P/D - polydispersity, Mw/Mn  
Ph - phenyl  
25 PMAO - see MAO  
PMMA - poly(methyl methacrylate)  
Pr - propyl  
PTFE - polytetrafluoroethylene  
RI - refractive index  
30 RT (or rt) - room temperature  
TCE - 1,1,2,2-tetrachloroethane  
Tc - temperature of crystallization  
Td - temperature of decomposition  
Tg - glass transition temperature  
35 TGA - Thermogravimetric Analysis  
THF - tetrahydrofuran  
Tm - melting temperature

TO - turnovers, the number of moles of monomer polymerized per g-atom of metal in the catalyst used

UV - ultraviolet

Unless otherwise noted, all pressures are gauge pressures.

In the Examples, the following procedure was used to quantitatively determine branching, and the distribution of branch sizes in the polymers (but not necessarily the simple number of branches as measured by total number of methyl groups per 1000 methylene groups). 100 MHz  $^{13}\text{C}$  NMR spectra were obtained on a Varian Unity 400 MHz spectrometer using a 10 mm probe on typically 15-20 wt% solutions of the polymers and 0.05 M Cr(acetylacetonate)<sub>3</sub> in 1,2,4-trichlorobenzene (TCB) unlocked at 120-140°C using a 90 degree pulse of 12.5 to 18.5  $\mu\text{sec}$ , a spectral width of 26 to 35 kHz, a relaxation delay of 5-9 s, an acquisition time of 0.64 sec and gated decoupling. Samples were preheated for at least 15 min before acquiring data. Data acquisition time was typically 12 hr. per sample. The  $T_1$  values of the carbons were measured under these conditions to be all less than 0.9 s. The longest  $T_1$  measured was for the Bu<sup>+</sup>, end of chain resonance at 14 ppm, which was 0.84 s. Occasionally about 16 vol. % benzene-d<sub>6</sub> was added to the TCB and the sample was run locked. Some samples were run in chloroform-d<sub>1</sub>, CDCl<sub>3</sub>-d<sub>1</sub>, (locked) at 30°C under similar acquisition parameters.  $T_1$ 's were also measured in CDCl<sub>3</sub> at ambient temperature on a typical sample with 0.05 M Cr(acetylacetonate)<sub>3</sub> to be all less than 0.68 s. In rare cases when Cr(acetylacetonate)<sub>3</sub> was not used, a 30-40 s recycle delay was used to insure quantitation. The glycidyl acrylate copolymer was run at 100°C with Cr(acetylacetonate)<sub>3</sub>. Spectra are referenced to the solvent - either the TCB highfield resonance at 127.8 ppm or the chloroform-d<sub>1</sub> triplet at 77 ppm. A DEPT 135 spectrum was done on most samples to distinguish methyls and methines from methylenes. Methyls were

distinguished from methines by chemical shift. EOC is end-of-chain. Assignments reference to following naming scheme:

1. xBy: By is a branch of length y carbons; x is  
5 the carbon being discussed, the methyl at the end of the branch is numbered 1. Thus the second carbon from the end of a butyl branch is 2B4. Branches of length y or greater are designated as y\*.
  2. xEBy: EB is an ester ended branch containing y  
10 methylenes. x is the carbon being discussed, the first methylene adjacent to the ester carbonyl is labeled 1. Thus the second methylene from the end of a 5 methylene ester terminated branch would be 2EB5. <sup>13</sup>C NMR of  
15 model compounds for EBy type branches for y=0 and y=5\* confirm the peak positions and assignments of these branches. In addition, a model compound for an EB1  
branch is consistent with 2 dimensional NMR data using the well know 2D NMR techniques of hsqc, hmbsc, and  
20 hsqc-tocsy; the 2D data confirms the presence of the EB5\*, EB0, EB1 and other intermediate length EB branches
  3. The methylenes in the backbone are denoted with Greek letters which determine how far from a  
25 branch point methine each methylene is. Thus ββ (beta beta) B denotes the central methylene in the following PCHRCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CHRP. Methylenes that are three or more carbons from a branch point are designated as γ\* (gamma\*).
  4. When x in xBy or xEBy is replaced by a M, the  
30 methine carbon of that branch is denoted.
- Integrals of unique carbons in each branch were measured and were reported as number of branches per 1000 methylenes (including methylenes in the backbone and branches). These integrals are accurate to +/- 5%  
35 relative for abundant branches and +/- 10 or 20% relative for branches present at less than 10 per 1000 methylenes.

Such types of analyses are generally known, see for instance "A Quantitative Analysis of Low Density (Branched) Polyethylenes by Carbon-13 Fourier Transform Nuclear Magnetic Resonance at 67.9 MHz", D. E. Axelson, et al., Macromolecules 12 (1979) pp. 41-52; "Fine Branching Structure in High-Pressure, Low Density Polyethylenes by 50.10-MHz  $^{13}\text{C}$  NMR Analysis", T. Usami et al., Macromolecules 17 (1984) pp. 1757-1761; and "Quantification of Branching in Polyethylene by  $^{13}\text{C}$  NMR Using Paramagnetic Relaxation Agents", J. V. Prasad, et al., Eur. Polym. J. 27 (1991) pp. 251-254 (Note that this latter paper is believed to have some significant typographical errors in it).

It is believed that in many of the polymers described herein which have unusual branching, i.e., they have more or fewer branches than would be expected for "normal" coordination polymerizations, or the distribution of sizes of the branches is different from that expected, that "branches on branches" are also present. By this is meant that a branch from the main chain on the polymer may itself contain one or more branches. It is also noted that the concept of a "main chain" may be a somewhat semantic argument if there are sufficient branches on branches in any particular polymer.

By a polymer hydrocarbyl branch is meant a methyl group to a methine or quaternary carbon atom or a group of consecutive methylenes terminated at one end by a methyl group and connected at the other end to a methine or quaternary carbon atom. The length of the branch is defined as the number of carbons from and including the methyl group to the nearest methine or quaternary carbon atom, but not including the methine or quaternary carbon atom. If the number of consecutive methylene groups is "n" then the branch contains (or the branch length is)  $n+1$ . Thus the structure (which represents part of a polymer) -

$\text{CH}_2\text{CH}_2\text{CH}[\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3]\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$  contains 2 branches, a methyl and an ethyl branch.

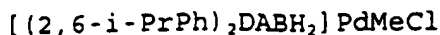
For ester ended branches a similar definition is used. An ester branch refers to a group of consecutive  
 5 methylene groups terminated at one end by an ester -  
 COOR group, and connected at the other end to a methine  
 or quaternary carbon atom. The length of the branch is  
 defined as the number of consecutive methylene groups  
 from the ester group to the nearest methine or  
 10 quaternary carbon atom, but not including the methine  
 or quaternary carbon atom. If the number of methylene  
 groups is "n", then the length of the branch is n.  
 Thus  $-\text{CH}_2\text{CH}_2\text{CH}[\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{COOR}]\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$   
 contains 2 branches, a methyl and an n=1 ester branch.

15 The  $^{13}\text{C}$  NMR peaks for copolymers of cyclopentene  
 and ethylene are described based on the labeling scheme  
 and assignments of A. Jerschow et al, *Macromolecules*  
 1995, 28, 7095-7099. The triads and pentads are  
 described as 1-cme, 1,3-ccmcc, 1,3-cmc, 2-cme, 2-cmc,  
 20 1,3-eme, 3-cme, and 4,5-cmc, where e = ethylene, c =  
 cyclopentene, and m = meta cyclopentene (i.e. 1,3  
 enchainment). The same labeling is used for  
 cyclopentene/1-pentene copolymer substituting p =  
 pentene for e. The synthesis of diimines is reported  
 25 in the literature (Tom Dieck, H.; Svoboda, M.; Grieser,  
 T. Z. *Naturforsch* 1981, 36b, 823-832. Kliegman, J. M.;  
 Barnes, R. K. *J. Org. Chem.* 1970, 35, 3140-3143.)

#### Example 1

30  $[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdMeCl}$   
 $\text{Et}_2\text{O}$  (75 mL) was added to a Schlenk flask  
 containing  $\text{CODPdMeCl}$  (COD = 1,5-cyclooctadiene) (3.53  
 g, 13.3 mmol) and a slight excess of  $(2,6\text{-i-PrPh})_2\text{DABMe}_2$   
 (5.43 g, 13.4 mmol, 1.01 equiv). An  
 orange precipitate began to form immediately upon  
 35 mixing. The reaction mixture was stirred overnight and  
 the  $\text{Et}_2\text{O}$  and free COD were then removed via filtration.  
 The product was washed with an additional 25 mL of  $\text{Et}_2\text{O}$   
 and then dried overnight in vacuo. A pale orange

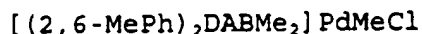
powder (7.18 g, 95.8%) was isolated:  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 400 MHz)  $\delta$  7.4 - 7.2 (m, 6,  $\text{H}_{\text{aryl}}$ ), 3.06 (septet, 2,  $J = 6.81$ ,  $\text{CHMe}_2$ ), 3.01 (septet, 2,  $J = 6.89$ ,  $\text{C}'\text{HMe}_2$ ), 2.04 and 2.03 ( $\text{N}=\text{C}(\text{Me})-\text{C}'(\text{Me})=\text{N}$ ), 1.40 (d, 6,  $J = 6.79$ ,  $\text{C}'\text{HMeMe}'$ ), 1.36 (d, 6,  $J = 6.76$ ,  $\text{CHMeMe}'$ ), 1.19 (d, 6,  $J = 6.83$ ,  $\text{CHMeMe}'$ ), 1.18 (d, 6,  $J = 6.87$ ,  $\text{C}'\text{HMeMe}'$ ), 0.36 (s, 3,  $\text{PdMe}$ );  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 400 MHz)  $\delta$  175.0 and 170.3 ( $\text{N}=\text{C}-\text{C}'=\text{N}$ ), 142.3 and 142.1 ( $\text{Ar}$ ,  $\text{Ar}'$ :  $\text{C}_{\text{ipso}}$ ), 138.9 and 138.4 ( $\text{Ar}$ ,  $\text{Ar}'$ :  $\text{C}_\text{O}$ ), 128.0 and 127.1 ( $\text{Ar}$ ,  $\text{Ar}'$ :  $\text{C}_\text{p}$ ), 124.3 and 123.5 ( $\text{Ar}$ ,  $\text{Ar}'$ :  $\text{C}_\text{m}$ ), 29.3 ( $\text{CHMe}_2$ ), 28.8 ( $\text{C}'\text{HMe}_2$ ), 23.9, 23.8, 23.5 and 23.3 ( $\text{CHMeMe}'$ ,  $\text{C}'\text{HMeMe}'$ ), 21.5 and 20.1 ( $\text{N}=\text{C}(\text{Me})-\text{C}'(\text{Me})=\text{N}$ ), 5.0 ( $J_{\text{CH}} = 135.0$ ,  $\text{PdMe}$ ).

Example 2

Following the procedure of Example 1, an orange powder was isolated in 97.1% yield:  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 400 MHz)  $\delta$  8.31 and 8.15 (s, 1 each,  $\text{N}=\text{C}(\text{H})-\text{C}'(\text{H})=\text{N}$ ), 7.3 - 7.1 (m, 6,  $\text{H}_{\text{aryl}}$ ), 3.22 (septet, 2,  $J = 6.80$ ,  $\text{CHMe}_2$ ), 3.21 (septet, 2,  $J = 6.86$ ,  $\text{C}'\text{HMe}_2$ ), 1.362, 1.356, 1.183 and 1.178 (d, 6 each,  $J = 7.75 - 6.90$ ;  $\text{CHMeMe}'$ ,  $\text{C}'\text{HMeMe}'$ ), 0.67 (s, 3,  $\text{PdMe}$ );  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 100 MHz)  $\delta$  164.5 ( $J_{\text{CH}} = 179.0$ ,  $\text{N}=\text{C}(\text{H})$ ), 160.6 ( $J_{\text{CH}} = 178.0$ ,  $\text{N}=\text{C}'(\text{H})$ ), 144.8 and 143.8 (Ar, Ar':  $\text{C}_{\text{ipso}}$ ), 140.0 and 139.2 (Ar, Ar':  $\text{C}_o$ ), 128.6 and 127.7 (Ar, Ar':  $\text{C}_p$ ), 124.0 and 123.4 (Ar, Ar':  $\text{C}_m$ ), 29.1 ( $\text{CHMe}_2$ ), 28.6 ( $\text{C}'\text{HMe}_2$ ), 24.7, 24.1, 23.1 and 22.7 ( $\text{CHMeMe}'$ ,  $\text{C}'\text{HMeMe}'$ ), 3.0 ( $J_{\text{CH}} = 134.0$ ,  $\text{PdMe}$ ). Anal. Calcd for  $(\text{C}_{27}\text{H}_{39}\text{ClN}_2\text{Pd})$ : C, 60.79; H, 7.37; N, 5.25. Found: C, 60.63; H, 7.24; N, 5.25.

Example 3

Following the procedure of Example 1, a yellow powder was isolated in 90.6% yield:  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 400 MHz)  $\delta$  7.3 - 6.9 (m, 6,  $\text{H}_{\text{aryl}}$ ), 2.22 (s, 6, Ar, Ar': Me), 2.00 and 1.97 ( $\text{N}=\text{C}(\text{Me})-\text{C}'(\text{Me})=\text{N}$ ), 0.25 (s, 3,  $\text{PdMe}$ ).

Example 4

Following the procedure of Example 1, an orange powder was isolated in 99.0% yield:  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 400 MHz, 41  $^\circ\text{C}$ )  $\delta$  8.29 and 8.14 ( $\text{N}=\text{C}(\text{H})-\text{C}'(\text{H})=\text{N}$ ), 7.2 - 7.1 (m, 6,  $\text{H}_{\text{aryl}}$ ), 2.33 and 2.30 (s, 6 each, Ar, Ar': Me), 0.61 (s, 3,  $\text{PdMe}$ );  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 100 MHz, 41  $^\circ\text{C}$ )  $\delta$  165.1 ( $J_{\text{CH}} = 179.2$ ,  $\text{N}=\text{C}(\text{H})$ ), 161.0 ( $J_{\text{CH}} = 177.8$ ,  $\text{N}=\text{C}'(\text{H})$ ), 147.3 and 146.6 (Ar, Ar':  $\text{C}_{\text{ipso}}$ ), 129.5 and 128.8 (Ar, Ar':  $\text{C}_o$ ), 128.8 and 128.5 (Ar, Ar':  $\text{C}_m$ ), 127.9 and 127.3 (Ar, Ar':  $\text{C}_p$ ), 18.7 and 18.2 (Ar, Ar': Me), 2.07 ( $J_{\text{CH}} = 136.4$ ,  $\text{PdMe}$ ).

Example 5

Following the procedure of Example 1, a yellow powder was isolated in 92.1% yield:  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 400 MHz)  $\delta$  7.29 (d, 2,  $J = 8.55$ , Ar:  $\text{H}_m$ ), 7.26 (d, 2,  $J = 7.83$ , Ar':  $\text{H}_m$ ), 6.90 (d, 2,  $J = 8.24$ , Ar':  $\text{H}_o$ ), 6.83 (d, 2,  $J = 8.34$ , Ar:  $\text{H}_o$ ), 2.39 (s, 6, Ar, Ar': Me), 2.15 and 2.05 (s, 3 each,  $\text{N}=\text{C}(\text{Me})-\text{C}'(\text{Me})=\text{N}$ ), 0.44 (s, 3, PdMe);  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 100 MHz)  $\delta$  176.0 and 169.9 (N=C-C'=N), 144.9 and 143.7 (Ar, Ar':  $\text{C}_{\text{ipso}}$ ), 137.0 and 136.9 (Ar, Ar':  $\text{C}_p$ ), 130.0 and 129.3 (Ar, Ar':  $\text{C}_m$ ), 122.0 and 121.5 (Ar, Ar':  $\text{C}_o$ ), 21.2 (N=C(Me)), 20.1 (Ar, Ar': Me), 19.8 (N=C'(Me)), 2.21 ( $J_{\text{CH}} = 135.3$ , PdMe). Anal. Calcd for  $(\text{C}_{19}\text{H}_{23}\text{ClN}_2\text{Pd})$ : C, 54.17; H, 5.50; N, 6.65. Found: C, 54.41; H, 5.37; N, 6.69.

Example 6

Following the procedure of Example 1, a burnt orange powder was isolated in 90.5% yield: Anal. Calcd for  $(\text{C}_{17}\text{H}_{19}\text{ClN}_2\text{Pd})$ : C, 51.93; H, 4.87; N, 7.12. Found: C, 51.36; H, 4.80; N, 6.82.

Example 7

$\text{Et}_2\text{O}$  (25 mL) was added to a mixture of  $[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdMeCl}$  (0.81 g, 1.45 mmol) and 0.5 equiv of NaBAF (0.64 g, 0.73 mmol) at room temperature. A golden yellow solution and NaCl precipitate formed immediately upon mixing. The reaction mixture was stirred overnight and then filtered. After the  $\text{Et}_2\text{O}$  was removed in vacuo, the product was washed with 25 mL of hexane. The yellow powder was then dissolved in 25 mL of  $\text{CH}_2\text{Cl}_2$  and the resulting solution was filtered in order to removed traces of unreacted NaBAF. Removal of  $\text{CH}_2\text{Cl}_2$  in vacuo yielded a golden yellow powder (1.25 g, 88.2%):  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 400 MHz)  $\delta$  7.73 (s, 8, BAF:  $\text{H}_o$ ), 7.57 (s, 4, BAF:  $\text{H}_p$ ), 7.33 (t, 2,  $J = 7.57$ , Ar:  $\text{H}_p$ ), 7.27 (d, 4,  $J = 7.69$ , Ar:  $\text{H}_o$ ), 7.18 (t, 2,  $J = 7.64$ , Ar:  $\text{H}_p$ ), 7.10 (d, 4,  $J = 7.44$ , Ar':  $\text{H}_o$ ), 2.88



(septet, 4,  $J = 6.80$ ,  $\text{CHMe}_2$ ), 2.75 (septet, 4,  $J = 6.82$ ,  $\text{C}'\text{HMe}_2$ ), 2.05 and 2.00 (s, 6 each,  $\text{N}=\text{C}(\text{Me})-\text{C}'(\text{Me})=\text{N}$ ), 1.22, 1.13, 1.08 and 1.01 (d, 12 each,  $J = 6.61-6.99$ ,  $\text{CHMeMe}'$ ,  $\text{C}'\text{HMeMe}'$ ), 0.41 (s, 6,  $\text{PdMe}$ );  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 100 MHz)  $\delta$  177.1 and 171.2 ( $\text{N}=\text{C}-\text{C}'=\text{N}$ ), 162.2 (q,  $J_{\text{BC}} = 49.8$ , BAF:  $\text{C}_{\text{ipso}}$ ), 141.4 and 141.0 (Ar, Ar':  $\text{C}_{\text{ipso}}$ ), 138.8 and 138.1 (Ar, Ar':  $\text{C}_o$ ), 135.2 (BAF:  $\text{C}_p$ ), 129.3 (q,  $J_{\text{CF}} = 31.6$ , BAF:  $\text{C}_m$ ), 128.6 and 127.8 (Ar, Ar':  $\text{C}_p$ ), 125.0 (q,  $J_{\text{CF}} = 272.5$ , BAF:  $\text{CF}_3$ ), 124.5 and 123.8 (Ar, Ar':  $\text{C}_m$ ), 117.9 (BAF:  $\text{C}_p$ ), 29.3 ( $\text{CHMe}_2$ ), 29.0 ( $\text{C}'\text{HMe}_2$ ), 23.8, 23.7, 23.6 and 23.0 ( $\text{CHMeMe}'$ ,  $\text{C}'\text{HMeMe}'$ ), 21.5 and 20.0 ( $\text{N}=\text{C}(\text{Me})-\text{C}'(\text{Me})=\text{N}$ ), 9.8 ( $J_{\text{CH}} = 136.0$ ,  $\text{PdMe}$ ). Anal. Calcd for ( $\text{C}_{90}\text{H}_{98}\text{BClF}_{24}\text{N}_4\text{Pd}_2$ ): C, 55.41; H, 5.06; N, 2.87. Found: C, 55.83; H, 5.09; N, 2.63.

#### Example 8



The procedure of Example 7 was followed with one exception, the removal of  $\text{CH}_2\text{Cl}_2$  in vacuo yielded a product that was partially an oil. Dissolving the compound in  $\text{Et}_2\text{O}$  and then removing the  $\text{Et}_2\text{O}$  in vacuo yielded a microcrystalline red solid (85.5%):  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 400 MHz)  $\delta$  8.20 and 8.09 (s, 2 each,  $\text{N}=\text{C}(\text{H})-\text{C}'(\text{H})=\text{N}$ ), 7.73 (s, 8, BAF:  $\text{H}_o$ ), 7.57 (s, 4, BAF:  $\text{H}_p$ ), 7.37 (t, 2,  $J = 7.73$ , Ar:  $\text{H}_p$ ), 7.28 (d, 4,  $J = 7.44$ , Ar:  $\text{H}_m$ ), 7.24 (t, 2, Ar':  $\text{H}_p$ ), 7.16 (d, 4,  $J = 7.19$ , Ar':  $\text{H}_m$ ), 3.04 (septet, 4,  $J = 6.80$ ,  $\text{CHMe}_2$ ), 2.93 (septet, 4,  $J = 6.80$ ,  $\text{C}'\text{HMe}_2$ ), 1.26 (d, 12,  $J = 6.79$ ,  $\text{CHMeMe}'$ ), 1.14 (d, 12,  $J = 6.83$ ,  $\text{CHMeMe}'$ ), 1.11 (d, 12,  $J = 6.80$ ,  $\text{C}'\text{HMeMe}'$ ), 1.06 (d, 12,  $J = 6.79$ ,  $\text{C}'\text{HMeMe}'$ ), 0.74 (s, 6,  $\text{PdMe}$ );  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 100 MHz)  $\delta$  166.0 ( $J_{\text{CH}} = 180.4$ ,  $\text{N}=\text{C}(\text{H})$ ), 161.9 (q,  $J_{\text{BC}} = 49.6$ , BAF:  $\text{C}_{\text{ipso}}$ ), 160.8 ( $J_{\text{CH}} = 179.9$ ,  $\text{N}=\text{C}'(\text{H})$ ), 143.5 and 143.0 (Ar, Ar':  $\text{C}_{\text{ipso}}$ ), 139.8 and 138.9 (Ar, Ar':  $\text{C}_o$ ), 135.2 (BAF:  $\text{C}_o$ ), 129.3 (q,  $J_{\text{CF}} = 31.4$ , BAF:  $\text{C}_m$ ), 129.3 and 128.5 (Ar, Ar':  $\text{C}_p$ ), 125.0 (q,  $J_{\text{CF}} = 272.4$ , BAF:  $\text{CF}_3$ ), 124.3 and 123.7 (Ar, Ar':  $\text{C}_m$ ), 117.9 (BAF:  $\text{C}_p$ ), 29.2 and 28.9 ( $\text{CHMe}_2$ ,  $\text{C}'\text{HMe}_2$ ), 24.5, 24.1, 23.0, and 22.5

(CHMeMe', C'HMeMe'), 10.3 (PdMe). Anal. Calcd for (C<sub>86</sub>H<sub>90</sub>BClF<sub>24</sub>N<sub>4</sub>Pd<sub>2</sub>): C, 54.52; H, 4.97; N, 2.96. Found: C, 54.97; H, 4.72; N, 2.71.

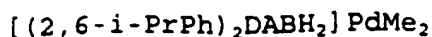
#### Example 9

- 5 Alternatively, the products of Examples 7 and 8 have been synthesized by stirring a 1:1 mixture of the appropriate PdMeCl compound and NaBAF in Et<sub>2</sub>O for ~1 h. Removal of solvent yields the dimer + 0.5 equiv of Na<sup>+</sup>(OEt<sub>2</sub>)<sub>2</sub>BAF<sup>-</sup>. Washing the product mixture with
- 10 hexane yields ether-free NaBAF, which is insoluble in CH<sub>2</sub>Cl<sub>2</sub>. Addition of CH<sub>2</sub>Cl<sub>2</sub> to the product mixture and filtration of the solution yields salt-free dimer: <sup>1</sup>H NMR spectral data are identical with that reported above.
- 15 For a synthesis of CODPdMe<sub>2</sub>, see: Rudler-Chauvin, M., and Rudler, H. J. Organomet. Chem. 1977, 134, 115-119.

#### Example 10

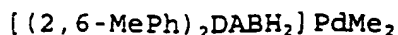
[(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>]PdMe<sub>2</sub>

- 20 A Schlenk flask containing a mixture of [(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>]PdMeCl (2.00 g, 3.57 mmol) and 0.5 equiv of Me<sub>2</sub>Mg (97.2 mg, 1.79 mmol) was cooled to -78 °C, and the reaction mixture was then suspended in 165 mL of Et<sub>2</sub>O. The reaction mixture was allowed to warm to room
- 25 temperature and then stirred for 2 h, and the resulting brown solution was then filtered twice. Cooling the solution to -30 °C yielded brown single crystals (474.9 mg, 24.6%, 2 crops): <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz) δ 7.2-7.1 (m, 6, H<sub>aryl</sub>), 3.17 (septet, 4, J = 6.92, CHMe<sub>2</sub>), 1.39 (d, 12, J = 6.74, CHMeMe'), 1.20 (N=C(Me)-C(Me)=N),
- 30 1.03 (d, 12, J = 6.89, CHMeMe'), 0.51 (s, 6, PdMe); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 100 MHz) δ 168.4 (N=C-C=N), 143.4 (Ar: C<sub>ipso</sub>), 138.0 (Ar: C<sub>o</sub>), 126.5 (Ar: C<sub>p</sub>), 123.6 (Ar: C<sub>m</sub>), 28.8 (CHMe<sub>2</sub>), 23.6 and 23.5 (CHMeMe'), 19.5 (N=C(Me)-C(Me)=N), -4.9 (J<sub>CH</sub> = 127.9, PdMe). Anal. Calcd for (C<sub>30</sub>H<sub>46</sub>N<sub>2</sub>Pd): C, 66.59; H, 8.57; N, 5.18. Found: C, 66.77; H, 8.62; N, 4.91.
- 35

Example 11

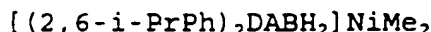
The synthesis of this compound in a manner analogous to Example 10, using 3.77 mmol of  $\text{ArN}=\text{C}(\text{H})-\text{C}(\text{H})=\text{NAr}$  and 1.93 mmol of  $\text{Me}_2\text{Mg}$  yielded 722.2 mg (37.4%) of a deep brown microcrystalline powder upon recrystallization of the product from a hexane/toluene solvent mixture.

This compound was also synthesized by the following method: A mixture of  $\text{Pd}(\text{acac})_2$  (2.66 g, 8.72 mmol) and corresponding diimine (3.35 g, 8.90 mmol) was suspended in 100 mL of  $\text{Et}_2\text{O}$ , stirred for 0.5 h at room temperature, and then cooled to  $-78^\circ\text{C}$ . A solution of  $\text{Me}_2\text{Mg}$  (0.499 g, 9.18 mmol) in 50 mL of  $\text{Et}_2\text{O}$  was then added via cannula to the cold reaction mixture. After stirring for 10 min at  $-78^\circ\text{C}$ , the yellow suspension was allowed to warm to room temperature and stirred for an additional hour. A second equivalent of the diimine was then added to the reaction mixture and stirring was continued for ~4 days. The brown  $\text{Et}_2\text{O}$  solution was then filtered and the solvent was removed in vacuo to yield a yellow-brown foam. The product was then extracted with 75 mL of hexane, and the resulting solution was filtered twice, concentrated, and cooled to  $-30^\circ\text{C}$  overnight to yield 1.43 g (32.0%) of brown powder:  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 400 MHz)  $\delta$  7.40 (s, 2,  $\text{N}=\text{C}(\text{H})-\text{C}(\text{H})=\text{N}$ ), 7.12 (s, 6,  $\text{H}_{\text{aryl}}$ ), 3.39 (septet, 4,  $J = 6.86$ ,  $\text{CHMe}_2$ ), 1.30 (d, 12,  $J = 6.81$ ,  $\text{CHMeMe}'$ ), 1.07 (d, 12,  $J = 6.91$ ,  $\text{CHMeMe}'$ ), 0.77 (s, 6,  $\text{PdMe}$ );  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 100 MHz)  $\delta$  159.9 ( $J_{\text{CH}} = 174.5$ ,  $\text{N}=\text{C}(\text{H})-\text{C}(\text{H})=\text{N}$ ), 145.7 (Ar:  $\text{C}_{\text{ipso}}$ ), 138.9 (Ar:  $\text{C}_o$ ), 127.2 (Ar:  $\text{C}_p$ ), 123.4 (Ar:  $\text{C}_m$ ), 28.5 ( $\text{CHMe}_2$ ), 24.4 and 22.8 ( $\text{CHMeMe}'$ ), -5.1 ( $J_{\text{CH}} = 128.3$ ,  $\text{PdMe}$ ). Anal. Calcd for  $(\text{C}_{28}\text{H}_{42}\text{N}_2\text{Pd})$ : C, 65.55, H, 8.25; N, 5.46. Found: C, 65.14; H, 8.12; N, 5.14.

Example 12

This compound was synthesized in a manner similar to the second procedure of Example 11 (stirred for 5 h at rt) using 5.13 mmol of the corresponding diimine and 2.57 mmol of  $\text{Me}_2\text{Mg}$ . After the reaction mixture was filtered, removal of  $\text{Et}_2\text{O}$  in vacuo yielded 1.29 g (62.2%) of a deep brown microcrystalline solid:  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 100 MHz,  $12^\circ\text{C}$ )  $\delta$  6.98 (s, 2,  $\text{N}=\text{C}(\text{H})-\text{C}(\text{H})=\text{N}$ ), 6.95 (s, 6,  $\text{H}_{\text{aryl}}$ ), 2.13 (s, 12, Ar: Me), 0.77 (s, 6, PdMe);  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 400 MHz,  $12^\circ\text{C}$ )  $\delta$  160.8 ( $\text{J}_{\text{CH}} = 174.6$ ,  $\text{N}=\text{C}(\text{H})-\text{C}(\text{H})=\text{N}$ ), 147.8 (Ar:  $\text{C}_{\text{ipso}}$ ), 128.2 (Ar:  $\text{C}_m$ ), 128.15 (Ar:  $\text{C}_o$ ), 126.3 (Ar:  $\text{C}_p$ ), 18.2 (Ar: Me), -5.5 ( $\text{J}_{\text{CH}} = 127.6$ , Pd-Me).

15

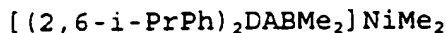
Example 13

The synthesis of this compound has been reported (Svoboda, M.; tom Dieck, H. J. *Organomet. Chem.* 1980, 191, 321-328) and was modified as follows: A mixture of  $\text{Ni}(\text{acac})_2$  (1.89 g, 7.35 mmol) and the corresponding diimine (2.83 g, 7.51 mmol) was suspended in 75 mL of  $\text{Et}_2\text{O}$  and the suspension was stirred for 1 h at room temperature. After cooling the reaction mixture to  $-78^\circ\text{C}$ , a solution of  $\text{Me}_2\text{Mg}$  (401 mg, 7.37 mmol) in 25 mL of  $\text{Et}_2\text{O}$  was added via cannula. The reaction mixture was stirred for 1 h at  $-78^\circ\text{C}$  and then for 2 h at  $0^\circ\text{C}$  to give a blue-green solution. After the solution was filtered, the  $\text{Et}_2\text{O}$  was removed in vacuo to give a blue-green brittle foam. The product was then dissolved in hexane and the resulting solution was filtered twice, concentrated, and then cooled to  $-30^\circ\text{C}$  to give 1.23 g (35.9% , one crop) of small turquoise crystals.

20

25

30

Example 14

The synthesis of this compound has been reported (Svoboda, M.; tom Dieck, H. J. *Organomet. Chem.* 1980, 191, 321-328) and was synthesized according to the above modified procedure (Example 13) using  $\text{Ni}(\text{acac})_2$

35

(3.02 g, 11.75 mmol), the corresponding diimine (4.80 g, 11.85 mmol) and  $\text{Me}_2\text{Mg}$  (640 mg, 11.77 mmol). A turquoise powder was isolated (620 mg, 10.7%).

#### Example 15

5  $\{[(2,6\text{-MePh})_2\text{DABMe}_2]\text{PdMe}(\text{MeCN})\}\text{BAF}^+$

To a mixture of  $\{[(2,6\text{-MePh})_2\text{DABMe}_2]\text{PdMeCl}\}$  (109.5 mg, 0.244 mmol) and NaBAF (216.0 mg, 0.244 mmol) were added 20 mL each of  $\text{Et}_2\text{O}$  and  $\text{CH}_2\text{Cl}_2$  and 1 mL of  $\text{CH}_3\text{CN}$ . The reaction mixture was then stirred for 1.5 h and then the NaCl was removed via filtration. Removal of the solvent in vacuo yielded a yellow powder, which was washed with 50 mL of hexane. The product (269.6 mg, 83.8%) was then dried in vacuo:  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 400 MHz)  $\delta$  7.73 (s, 8, BAF:  $\text{H}_\text{O}$ ), 7.57 (s, 4, BAF:  $\text{H}_\text{P}$ ), 7.22-7.16 (m, 6,  $\text{H}_{\text{aryl}}$ ), 2.23 (s, 6, Ar: Me), 2.17 (s, 6, Ar': Me), 2.16, 2.14, and 1.79 (s, 3 each,  $\text{N}=\text{C}(\text{Me})-\text{C}'(\text{Me})=\text{N}$ , NCMe), 0.38 (s, 3, PdMe);  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 100 MHz)  $\delta$  180.1 and 172.2 ( $\text{N}=\text{C}-\text{C}'=\text{N}$ ), 162.1 (q,  $J_{\text{BC}} = 49.9$ , BAF:  $\text{C}_{\text{ipso}}$ ), 142.9 (Ar, Ar':  $\text{C}_\text{O}$ ), 135.2 (BAF:  $\text{C}_\text{O}$ ), 129.3 (Ar:  $\text{C}_\text{m}$ ), 129.2 (q,  $J_{\text{CF}} = 30.6$ , BAF:  $\text{C}_\text{m}$ ), 129.0 (Ar':  $\text{C}_\text{m}$ ), 128.4 (Ar:  $\text{C}_\text{p}$ ), 128.2 (Ar:  $\text{C}_\text{O}$ ), 127.7 (Ar':  $\text{C}_\text{p}$ ), 127.4 (Ar':  $\text{C}_\text{O}$ ), 125.0 (q,  $J_{\text{CF}} = 272.4$ , BAF:  $\text{CF}_3$ ), 121.8 (NCMe), 117.9 (BAF:  $\text{C}_\text{p}$ ), 20.2 and 19.2 ( $\text{N}=\text{C}(\text{Me})-\text{C}'(\text{Me})=\text{N}$ ), 18.0 (Ar: Me), 17.9 (Ar': Me), 5.1 and 2.3 (NCMe, PdMe). Anal. Calcd for  $(\text{C}_{55}\text{H}_{42}\text{BF}_{24}\text{N}_3\text{Pd})$ : C, 50.12; H, 3.21; N, 3.19. Found: C, 50.13; H, 3.13, N, 2.99.

#### Example 16

30  $\{[(4\text{-MePh})_2\text{DABMe}_2]\text{PdMe}(\text{MeCN})\}\text{BAF}^+$

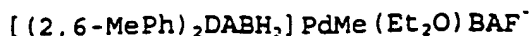
Following the procedure of Example 15, a yellow powder was isolated in 85% yield:  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 400 MHz)  $\delta$  7.81 (s, 8, BAF:  $\text{H}_\text{O}$ ), 7.73 (s, 4, BAF:  $\text{H}_\text{P}$ ), 7.30 (d, 4,  $J = 8.41$ , Ar, Ar':  $\text{H}_\text{m}$ ), 6.89 (d, 2,  $J = 8.26$ , Ar:  $\text{H}_\text{O}$ ), 6.77 (d, 2,  $J = 8.19$ , Ar':  $\text{H}_\text{O}$ ), 2.39 (s, 6, Ar, Ar': Me), 2.24, 2.17 and 1.93 (s, 3 each,  $\text{N}=\text{C}(\text{Me})-\text{C}'(\text{Me})=\text{N}$ , NCMe)Pd-Me;  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 100 MHz)  $\delta$  180.7 and 171.6 ( $\text{N}=\text{C}-\text{C}'=\text{N}$ ), 162.1 (q,  $J_{\text{BC}} = 49.8$ , BAF:  $\text{C}_{\text{ipso}}$ ), 143.4 and 142.9 (Ar, Ar':  $\text{C}_{\text{ipso}}$ ), 138.6 and 138.5 (Ar,

Ar': C<sub>p</sub>), 135.2 (BAF: C<sub>o</sub>), 130.6 and 130.4 (Ar, Ar': C<sub>m</sub>), 129.3 (q, J<sub>CF</sub> = 31.6, BAF: C<sub>m</sub>), 125.0 (q, J<sub>CF</sub> = 272.5, BAF: CF<sub>3</sub>), 122.1 (NCMe), 121.0 and 120.9 (Ar, Ar': C<sub>o</sub>), 117.9 (BAF: C<sub>p</sub>), 21.5 (ArN=C(Me)), 21.1 (Ar, Ar': Me), 19.7 (ArN=C'(Me)), 6.2 and 3.0 (NCMe, PdMe).  
 5 Anal. Calcd for (C<sub>53</sub>H<sub>38</sub>BF<sub>24</sub>N<sub>3</sub>Pd): C, 49.34; H, 2.97; N, 3.26. Found: C, 49.55; H, 2.93; N, 3.10.

#### Example 17

[(2,6-MePh)<sub>2</sub>DABMe<sub>2</sub>]PdMe(Et<sub>2</sub>O)BAF<sup>-</sup>

10 A Schlenk flask containing a mixture of [(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>]PdMe<sub>2</sub> (501 mg, 0.926 mmol) and H<sup>+</sup>(OEt<sub>2</sub>)<sub>2</sub>BAF<sup>-</sup> (938 mg, 0.926 mmol) was cooled to -78°C. Following the addition of 50 mL of Et<sub>2</sub>O, the solution  
 15 was allowed to warm and stirred briefly (~15 min) at room temperature. The solution was then filtered and the solvent was removed in vacuo to give a pale orange powder (1.28 g, 94.5%), which was stored at -30°C under an inert atmosphere: <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz, -60°C) δ 7.71 (s, 8, BAF: H<sub>O</sub>), 7.58 (s, 4, BAF: H<sub>p</sub>), 7.4 - 7.0  
 20 (m, 6, H<sub>aryl</sub>), 3.18 (q, 4, J = 7.10, O(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 2.86 (septet, 2, J = 6.65, CHMe<sub>2</sub>), 2.80 (septet, 2, J = 6.55, C' HMe<sub>2</sub>), 2.18 and 2.15 (N=C(Me)-C'(Me)=N), 1.34, 1.29, 1.14 and 1.13 (d, 6 each, J = 6.4-6.7, CHMeMe', C' HMeMe'), 1.06 (t, J = 6.9, O(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 0.33 (s, 3, PdMe); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100 MHz, -60°C) δ 179.0 and  
 25 172.1 (N=C-C'=N), 161.4 (q, J<sub>BC</sub> = 49.7, BAF: C<sub>ipso</sub>), 140.21 and 140.15 (Ar, Ar': C<sub>ipso</sub>), 137.7 and 137.4 (Ar, Ar': C<sub>o</sub>), 134.4 (BAF: C<sub>p</sub>), 128.3 (q, J<sub>CF</sub> = 31.3, BAF: C<sub>m</sub>), 128.5 and 128.2 (Ar, Ar': C<sub>p</sub>), 124.2 (q, J<sub>CF</sub>  
 30 = 272.4, BAF: CF<sub>3</sub>), 117.3 (BAF: C<sub>p</sub>), 71.5 (O(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 28.7 (CHMe<sub>2</sub>), 28.4 (C' HMe<sub>2</sub>), 23.7, 23.6, 23.1 and 22.6 (CHMeMe', C' HMeMe'), 21.5 and 20.7 (N=C(Me)-C'(Me)=N), 14.2 (O(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>, 8.6 (PdMe). Anal. Calcd for (C<sub>65</sub>H<sub>65</sub>BF<sub>24</sub>N<sub>2</sub>OPd): C, 53.35; H, 4.48; N, 1.91. Found:  
 35 C, 53.01; H, 4.35; N, 1.68.

Example 18

- Following the procedure of Example 17, an orange powder was synthesized in 94.3% yield and stored at -30°C:
- <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz, -60°C) δ 8.23 and 8.20 (s, 1 each, N=C(H)-C'(H)=N), 7.72 (s, 8, BAF: H<sub>O</sub>), 7.54 (s, 4, BAF: H<sub>p</sub>), 7.40 - 7.27 (m, 6, H<sub>aryl</sub>), 3.32 (q, 4, J = 6.90, O(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 3.04 and 3.01 (septets, 2 each, J = 6.9 - 7.1, CHMe<sub>2</sub> and C'HMe<sub>2</sub>), 1.32, 1.318, 1.14 and 1.10 (d, 6 each, J = 6.5 - 6.8, CHMeMe' and C'HMeMe'), 1.21 (t, 6, J = 6.93, O(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 0.70 (s, 3, PdMe);
- <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100 MHz, -60°C) δ 166.9 (J<sub>CH</sub> = 182.6, N=C(H)), 161.5 (J<sub>BC</sub> = 49.7, BAF: C<sub>ipso</sub>), 161.3 (J<sub>CH</sub> = 181.6, N=C'(H)), 143.0 and 141.8 (Ar, Ar': C<sub>ipso</sub>), 138.7 and 137.8 (Ar, Ar': C<sub>O</sub>), 134.4 (BAF: C<sub>O</sub>), 129.1 and 128.8 (Ar, Ar': C<sub>p</sub>), 128.3 (J<sub>CF</sub> = 31.3, BAF: C<sub>m</sub>), 124.0 and 123.9 (Ar, Ar': C<sub>m</sub>), 117.3 (BAF: C<sub>p</sub>), 72.0 (O(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 28.5 and 28.4 (CHMe<sub>2</sub>, C'HMe<sub>2</sub>), 25.2, 24.1, 21.9 and 21.7 (CHMeMe', C'HMeMe'), 15.2 (O(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 11.4 (J<sub>CH</sub> = 137.8, PdMe). Anal. Calcd for (C<sub>63</sub>H<sub>61</sub>BF<sub>24</sub>N<sub>2</sub>OPd): C, 52.72; H, 4.28; N, 1.95. Found: C, 52.72; H, 4.26; N, 1.86.

Example 19

- Following the procedure of Example 17, a magenta powder was isolated and stored at -30°C: <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz, -60°C; A H<sub>2</sub>O adduct and free Et<sub>2</sub>O were observed.) δ 7.73 (s, 8, BAF: H<sub>O</sub>), 7.55 (s, 4, BAF: H<sub>p</sub>), 7.4 - 7.2 (m, 6, H<sub>aryl</sub>), 3.42 (s, 2, OH<sub>2</sub>), 3.22 (q, 4, O(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 3.14 and 3.11 (septets, 2 each, J = 7.1, CHMe<sub>2</sub>, C'HMe<sub>2</sub>), 1.95 and 1.78 (s, 3 each, N=C(Me)-C'(Me)=N), 1.42, 1.39, 1.18 and 1.11 (d, 6 each, J = 6.6 - 6.9, CHMeMe' and C'HMeMe'), 0.93 (t, J = 7.5, O(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), -0.26 (s, 3, NiMe); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100 MHz, -58°C) δ 175.2 and 170.7 (N=C-C'=N), 161.6 (q, J<sub>BC</sub> = 49.7, BAF: C<sub>ipso</sub>), 141.2 (Ar: C<sub>ipso</sub>), 139.16 and 138.68 (Ar, Ar': C<sub>O</sub>), 136.8 (Ar': C<sub>ipso</sub>), 134.5 (BAF: C<sub>O</sub>), 129.1 and 128.4 (Ar, Ar': C<sub>p</sub>), 128.5

(q,  $J_{CF} = 32.4$ , BAF:  $C_m$ ), 125.0 and 124.2 (Ar, Ar':  $C_m$ ), 124.3 (q,  $J_{CF} = 272.5$ , BAF:  $CF_3$ ), 117.4 (BAF:  $C_p$ ), 66.0 ( $O(CH_2CH_3)_2$ ), 29.1 ( $CHMe_2$ ), 28.9 ( $C'HMe_2$ ), 23.51, 23.45, 23.03, and 22.95 ( $CHMeMe'$ ,  $C'HMeMe'$ ), 21.0 and 19.2 ( $N=C(Me)-C'(Me)=N$ ), 14.2 ( $OCH_2CH_3$ ), -0.86 ( $J_{CH} = 131.8$ , NiMe). Anal. Calcd for  $(C_{65}H_{65}BF_{24}N_2NiO)$ : C, 55.15; H, 4.63; N, 1.98. Found: C, 54.74; H, 4.53; N, 2.05.

#### Example 20

10  $[(2,6-MePh)_2DABH_2]NiMe(Et_2O)BAF$

Following the procedure of Example 17, a purple powder was obtained and stored at  $-30^\circ C$ :  $^1H$  NMR ( $CD_2Cl_2$ , 400 MHz,  $-80^\circ C$ ;  $H_2O$  and  $Et_2O$  adducts were observed in an 80:20 ratio, respectively.)  $\delta$  8.31 and 8.13 (s, 0.8 each,  $N=C(H)-C'(H)=N$ ;  $H_2O$  Adduct), 8.18 and 8.00 (s, 0.2 each,  $N=C(H)-C'(H)=N$ ;  $Et_2O$  Adduct), 7.71 (s, 8 BAF:  $C_o$ ), 7.53 (s, 4, BAF:  $C_p$ ), 7.5 - 7.0 (m, 6,  $H_{aryl}$ ), 4.21 (s, 1.6,  $OH_2$ ), 3.5 - 3.1 (m, 8,  $O(CH_2CH_3)_2$ ,  $CHMe_2$ ,  $C'HMe_2$ ), 1.38, 1.37, 1.16 and 1.08 (d, 4.8 each,  $CHMeMe'$ ,  $C'HMeMe'$ ;  $H_2O$  Adduct; These peaks overlap with and obscure the  $CHMe_2$  doublets of the  $Et_2O$  adduct.), 0.27 (s, 2.4,  $PdMe$ ;  $H_2O$  Adduct), 0.12 (s, 0.6,  $PdMe$ :  $Et_2O$  Adduct).

#### Examples 21-23

25 The rate of exchange of free and bound ethylene was determined by  $^1H$  NMR line broadening experiments at  $-85^\circ C$  for complex (XI), see the Table below. The NMR instrument was a 400 MHz Varian® NMR spectrometer. Samples were prepared according to the following procedure: The palladium ether adducts  $\{[(2,6-i-PrPh)_2DABMe_2]PdMe(OEt_2)\}BAF$ ,  $\{[(2,6-i-PrPh)_2An]PdMe(OEt_2)\}BAF$ , and  $\{[(2,6-i-PrPh)_2DABH_2]PdMe(OEt_2)\}BAF$  were used as precursors to (XI), and were weighed (~15 mg) in a tared 5 mm dia. NMR tube in a nitrogen-filled drybox. The tube was then capped with a septum and Parafilm® and cooled to  $-80^\circ C$ . Dry, degassed  $CD_2Cl_2$  (700  $\mu L$ ) was then added to the palladium complex via gastight syringe, and the



tube was shaken and warmed briefly to give a homogeneous solution. After acquiring a  $-85^{\circ}\text{C}$  NMR spectrum, ethylene was added to the solution via gastight syringe and a second NMR spectrum was acquired at  $-85^{\circ}\text{C}$ . The molarity of the BAF counterion was calculated according to the moles of the ether adduct placed in the NMR tube. The molarity of (XI) and free ethylene were calculated using the BAF peaks as an internal standard. Line-widths (W) were measured at half-height in units of Hz for the complexed ethylene signal (usually at 5 to 4 ppm) and were corrected for line widths ( $W_0$ ) in the absence of exchange.

For (XI) the exchange rate was determined from the standard equation for the slow exchange approximation:

$$k = (W - W_0)\pi/[=],$$

where [=] is the molar concentration of ethylene.

These experiments were repeated twice and an average value is reported below.

Rate Constants for Ethylene Exchange<sup>a</sup>

Ex.	(XI)	k ( $\text{L}\cdot\text{M}^{-1}\cdot\text{s}^{-1}$ )
21	$\{[(2,6\text{-}i\text{-PrPh})_2\text{DABMe}_2]\text{PdMe}(=)\}\text{BAF}$	45
22	$\{[(2,6\text{-}i\text{-PrPh})_2\text{An}]\text{PdMe}(=)\}\text{BAF}$	520
23	$\{[(2,6\text{-}i\text{-PrPh})_2\text{DABH}_2]\text{PdMe}(=)\}\text{BAF}$	8100

<sup>a</sup>The  $T_1$  of free ethylene is 15 sec. A pulse delay of 60 sec and a  $30^{\circ}$  pulse width were used.

#### Example 24

Anhydrous  $\text{FeCl}_2$  (228 mg, 1.8 mmol) and (2,6-*i*-PrPh)<sub>2</sub>DABAn (1.0 g, 2.0 mmol) were combined as solids and dissolved in 40 ml of  $\text{CH}_2\text{Cl}_2$ . The mixture was stirred at  $25^{\circ}\text{C}$  for 4 hr. The resulting green solution was removed from the unreacted  $\text{FeCl}_2$  via filter cannula. The solvent was removed under reduced

pressure resulting in a green solid (0.95 g, 84% yield).

A portion of the green solid (40 mg) was immediately transferred to another Schlenk flask and dissolved in 50 ml of toluene under 1 atm of ethylene. The solution was cooled to 0°C, and 6 ml of a 10% MAO solution in toluene was added. The resulting purple solution was warmed to 25°C and stirred for 11 hr. The polymerization was quenched and the polymer precipitated by acetone. The resulting polymer was washed with 6M HCl, water and acetone. Subsequent drying of the polymer resulted in 60 mg of white polyethylene. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz) δ 1.25 (CH<sub>2</sub>, CH) δ 0.85 (m, CH<sub>3</sub>).

#### Example 25

(2-t-BuPh)<sub>2</sub>DABMe<sub>2</sub>

A Schlenk tube was charged with 2-t-butylaniline (5.00 mL, 32.1 mmol) and 2,3-butanedione (1.35 mL, 15.4 mmol). Methanol (10 mL) and formic acid (1 mL) were added and a yellow precipitate began to form almost immediately upon stirring. The reaction mixture was allowed to stir overnight. The resulting yellow solid was collected via filtration and dried under vacuum. The solid was dissolved in ether and dried over Na<sub>2</sub>SO<sub>4</sub> for 2-3 h. The ether solution was filtered, condensed and placed into the freezer (-30°C). Yellow crystals were isolated via filtration and dried under vacuum overnight (4.60 g, 85.7%): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz) δ 7.41 (dd, 2H, J = 7.7, 1.5 Hz, H<sub>m</sub>), 7.19 (td, 2H, J = 7.5, 1.5 Hz, H<sub>m</sub> or H<sub>p</sub>), 7.07 (td, 2H, J = 7.6, 1.6 Hz, H<sub>m</sub> or H<sub>p</sub>), 6.50 (dd, 2H, J = 7.7, 1.8 Hz, H<sub>o</sub>), 2.19 (s, 6H, N=C(Me)-C(Me)=N), 1.34 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>).

#### Examples 26 and 27

General Polymerization Procedure for Examples 26 and 27: In the drybox, a glass insert was loaded with [(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)Pd(μ-Cl)]<sub>2</sub> (11 mg, 0.03 mmol), NaBAF (53 mg, 0.06 mmol), and an α-diimine ligand (0.06 mmol). The insert was cooled to -35°C in the drybox freezer, 5 mL

of C<sub>6</sub>D<sub>6</sub> was added to the cold insert, and the insert was then capped and sealed. Outside of the drybox, the cold tube was placed under 6.9 MPa of ethylene and allowed to warm to RT as it was shaken mechanically for 18 h. An aliquot of the solution was used to acquire a <sup>1</sup>H NMR spectrum. The remaining portion was added to ~20 mL of MeOH in order to precipitate the polymer. The polyethylene was isolated and dried under vacuum

Example 26

α-Diimine was (2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>. Polyethylene (50 mg) was isolated as a solid. <sup>1</sup>H NMR spectrum (C<sub>6</sub>D<sub>6</sub>) is consistent with the production of 1- and 2-butenes and branched polyethylene.

Example 27

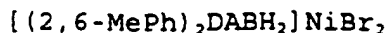
α-Diimine was (2,6-i-PrPh)<sub>2</sub>DABAn. Polyethylene (17 mg) was isolated as a solid. <sup>1</sup>H NMR spectrum (C<sub>6</sub>D<sub>6</sub>) is consistent with the production of branched polyethylene.

Example 28

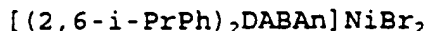
[(2,6-i-PrPh)<sub>2</sub>DABH<sub>2</sub>]NiBr<sub>2</sub>  
The corresponding diimine (980 mg, 2.61 mmol) was dissolved in 10 mL of CH<sub>2</sub>Cl<sub>2</sub> in a Schlenk tube under a N<sub>2</sub> atmosphere. This solution was added via cannula to a suspension of (DME)NiBr<sub>2</sub> (DME = 1,2-dimethoxyethane) (787 mg, 2.55 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL). The resulting red/brown mixture was stirred for 20 hours. The solvent was evaporated under reduced pressure resulting in a red/brown solid. The product was washed with 3 x 10 mL of hexane and dried in vacuo. The product was isolated as a red/brown powder (1.25 g, 82% yield).

Example 29

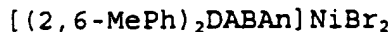
[(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>]NiBr<sub>2</sub>  
Using a procedure similar to that of Example 28, 500 mg (1.62 mmol) (DME)NiBr<sub>2</sub> and 687 mg (1.70 mmol) of the corresponding diimine were combined. The product was isolated as an orange/brown powder (670 mg, 67% yield).

Example 30

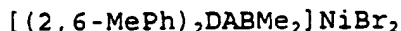
Using a procedure similar to that of Example 28, 500 mg (1.62 mmol) (DME)NiBr<sub>2</sub> and 448 mg (1.70 mmol) of the corresponding diimine were combined. The product was isolated as a brown powder (622 mg, 80% yield).

Example 31

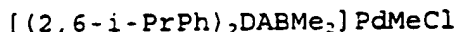
Using a procedure similar to that of Example 28, 500 mg (1.62 mmol) (DME)NiBr<sub>2</sub> and 850 mg (1.70 mmol) of the corresponding diimine were combined. The product was isolated as a red powder (998 mg, 86% yield). Anal. Calcd. for C<sub>36</sub>H<sub>40</sub>N<sub>2</sub>Br<sub>2</sub>Ni: C, 60.12; H, 5.61; N, 3.89. Found C, 59.88; H, 5.20; N, 3.52.

Example 32

The corresponding diimine (1.92 g, 4.95 mmol) and (DME)NiBr<sub>2</sub> (1.5 g, 4.86 mmol) were combined as solids in a flame dried Schlenk under an argon atmosphere. To this mixture 30 mL of CH<sub>2</sub>Cl<sub>2</sub> was added giving an orange solution. The mixture was stirred for 18 hours resulting in a red/brown suspension. The CH<sub>2</sub>Cl<sub>2</sub> was removed via filter cannula leaving a red/brown solid. The product was washed with 2 x 10 mL of CH<sub>2</sub>Cl<sub>2</sub> and dried under vacuum. The product was obtained as a red/brown powder (2.5 g, 83% yield).

Example 33

Using a procedure similar to that of Example 32, the title compound was made from 1.5 g (4.86 mmol) (DME)NiBr<sub>2</sub> and 1.45 g (4.95 mmol) of the corresponding diimine. The product was obtained as a brown powder (2.05 g, 81% yield).

Example 34

(COD)PdMeCl (9.04 g, 34.1 mmol) was dissolved in 200 ml of methylene chloride. To this solution was added the corresponding diimine (13.79 g, 34.1 mmol).

The resulting solution rapidly changed color from yellow to orange-red. After stirring at room temperature for several hours it was concentrated to form a saturated solution of the desired product, and cooled to  $-40^{\circ}\text{C}$  overnight. An orange solid crystallized from the solution, and was isolated by filtration, washed with petroleum ether, and dried to afford 12.54 g of the title compound as an orange powder. Second and third crops of crystals obtained from the mother liquor afforded an additional 3.22 g of product. Total yield = 87%.

#### Examples 35-39

The following compounds were made by a method similar to that used in Example 34.

Example	Compound
35	$[(2,6\text{-i-PrPh})_2\text{DABH}_2]\text{PdMeCl}$
36	$[(2,6\text{-i-PrPh})_2\text{DABAn}]\text{PdMeCl}$
37	$[(\text{Ph})_2\text{DABMe}_2]\text{PdMeCl}$
38	$[(2,6\text{-EtPh})_2\text{DABMe}_2]\text{PdMeCl}$
39	$[(2,4,6\text{-MePh})_2\text{DABMe}_2]\text{PdMeCl}$

Note: The diethyl ether complexes described in Examples 41-46 are unstable in non-coordinating solvents such as methylene chloride and chloroform. They are characterized by  $^1\text{H}$  NMR spectra recorded in  $\text{CD}_3\text{CN}$ ; under these conditions the acetonitrile adduct of the Pd methyl cation is formed. Typically, less than a whole equivalent of free diethylether is observed by  $^1\text{H}$  NMR when  $[(\text{R})_2\text{DAB}(\text{R}')_2]\text{PdMe}(\text{OEt}_2)\text{X}$  is dissolved in  $\text{CD}_3\text{CN}$ . Therefore, it is believed the complexes designated as " $\{[(\text{R})_2\text{DAB}(\text{R}')_2]\text{PdMe}(\text{OEt}_2)\}\text{X}$ " below are likely mixtures of  $\{[(\text{R})_2\text{DAB}(\text{R}')_2]\text{PdMe}(\text{OEt}_2)\}\text{X}$  and  $[(\text{R})_2\text{DAB}(\text{R}')_2]\text{PdMeX}$ , and in the latter complexes the X ligand ( $\text{SbF}_6$ ,  $\text{BF}_4$ , or  $\text{PF}_6$ ) is weakly coordinated to palladium. A formula of the type " $\{[(\text{R})_2\text{DAB}(\text{R}')_2]\text{PdMe}(\text{OEt}_2)\}\text{X}$ " is a "formal" way of conveying the approximate overall composition of

this compound, but may not accurately depict the exact coordination to the metal atom.

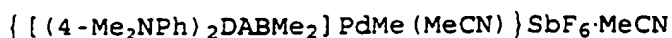
Listed below are the  $^{13}\text{C}$  NMR data for Example 36.

5

 $^{13}\text{C}$  NMR data

TCB, 120C, 0.05M CrAcAc

<u>freq ppm</u>	<u>intensity</u>	
46.5568	24.6005	1 cmp and/or 1,3 ccmcc
44.9321	3.42517	1,3 cmc
40.8118	55.4341	2 pmp
40.3658	145.916	1,3 pmp
39.5693	18.458	methylenes from 2 cmp and/or 2 cmc
38.7782	4.16118	
38.6295	5.84037	
38.2844	8.43098	
38.1198	8.29802	
37.8384	3.83966	
37.5198	13.4977	
37.2384	23.4819	
37.1163	16.8339	
36.7446	114.983	
36.0012	6.19217	
35.7198	5.17495	
34.2278	4.83958	
32.9216	20.2781	3B <sub>6</sub> <sup>+</sup> , 3EOC
32.619	3.6086	
32.4172	2.98497	
32.1995	10.637	
31.9765	42.2547	
31.8809	143.871	
30.4686	27.9974	
30.3199	47.1951	
30.0225	36.1409	
29.7411	102.51	
29.311	4.83244	
28.7111	117.354	
28.2597	9.05515	
27.1659	22.5725	
27.0067	5.81855	
26.1146	13.5772	
24.5642	2.59695	$\beta\beta\text{B}^{\text{B}}$
22.6368	12.726	2B <sub>5</sub> <sup>+</sup> , 2EOC
20.1413	3.7815	2B <sub>3</sub>
19.7271	20.0959	1B <sub>1</sub>
17.5236	7.01554	end group
14.2528	3.03535	1B <sub>3</sub>
13.8812	12.3635	1B <sub>4</sub> <sup>+</sup> , 1EOC

Example 40

A procedure analogous to that used in Example 54, using (4-Me<sub>2</sub>NPh)<sub>2</sub>DABMe<sub>2</sub> in place of (2-C<sub>6</sub>H<sub>4</sub>-<sup>t</sup>Bu)<sub>2</sub>DABMe<sub>2</sub>, afforded {[(4-NMe<sub>2</sub>Ph)<sub>2</sub>DABMe<sub>2</sub>]PdMe(MeCN)}SbF<sub>6</sub>·MeCN as a purple solid (product was not recrystallized in this instance). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 6.96 (d, 2H, H<sub>aryl</sub>), 6.75 (mult, 6H, H<sub>aryl</sub>), 3.01 (s, 6H, NMe<sub>2</sub>), 2.98 (s, 6H, NMe'<sub>2</sub>), 2.30, 2.18, 2.03, 1.96 (s's, 3H each, N=CMe, N=CMe', and free and coordinated N≡CMe), 0.49 (s, 3H, Pd-Me).

10

Example 41

{[(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>]PdMe(Et<sub>2</sub>O)<sub>n</sub>}SbF<sub>6</sub><sup>-</sup>  
[(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>]PdMeCl (0.84 g, 1.49 mmol) was suspended in 50 mL of diethylether and the mixture cooled to -40°C. To this was added AgSbF<sub>6</sub> (0.52 g, 1.50 mmol). The reaction mixture was allowed to warm to room temperature, and stirred at room temperature for 90 min. The reaction mixture was then filtered, giving a pale yellow filtrate and a bright yellow precipitate. The yellow precipitate was extracted with 4 x 20 mL 50/50 methylene chloride/diethyl ether. The filtrate and extracts were then combined with an additional 30 mL diethyl ether. The resulting solution was then concentrated to half its original volume and 100 mL of petroleum ether added. The resulting precipitate was filtered off and dried, affording 1.04 g of the title compound as a yellow-orange powder (83% yield). <sup>1</sup>H NMR (CD<sub>3</sub>CN) δ 7.30 (mult, 6H, H<sub>aryl</sub>), 3.37 [q, free O(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>], 3.05-2.90 (overlapping sept's, 4H, CHMe<sub>2</sub>), 2.20 (s, 3H, N=CMe), 2.19 (s, 3H, N=CMe'), 1.35-1.14 (overlapping d's, 24H, CHMe<sub>2</sub>), 1.08 (t, free O(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 0.28 (s, 3H, Pd-Me). This material contained 0.4 equiv of Et<sub>2</sub>O per Pd, as determined by <sup>1</sup>H NMR integration.

20

25

30

Example 42

35



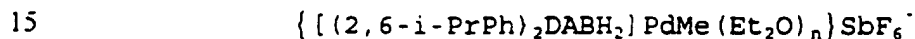
A procedure analogous to that used in Example 41, using AgBF<sub>4</sub> in place of AgSbF<sub>6</sub>, afforded the title compound as a mustard yellow powder in 61% yield. This

material contained 0.3 equiv of Et<sub>2</sub>O per Pd, as determined by <sup>1</sup>H NMR integration. <sup>1</sup>H NMR in CD<sub>3</sub>CN was otherwise identical to that of the compound made in Example 41.

5

Example 43

A procedure analogous to that used in Example 41, using AgPF<sub>6</sub> in place of AgSbF<sub>6</sub>, afforded the title compound as a yellow-orange powder in 72% yield. This material contained 0.4 equiv of Et<sub>2</sub>O per Pd, as determined by <sup>1</sup>H NMR integration. <sup>1</sup>H NMR in CD<sub>3</sub>CN was identical to that of the compound of Example 41.

Example 44

A procedure analogous to that used in Example 41, using [(2,6-*i*-PrPh)<sub>2</sub>DABH<sub>2</sub>]PdMeCl in place of [(2,6-*i*-PrPh)<sub>2</sub>DABMe<sub>2</sub>]PdMeCl, afforded the title compound in 71% yield. <sup>1</sup>H NMR (CD<sub>3</sub>CN) δ 8.30 (s, 2H, N=CH and N=CH'), 7.30 (s, 6H, H<sub>aryl</sub>), 3.37 [q, free O(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>], 3.15 (br, 4H, CHMe<sub>2</sub>), 1.40-1.10 (br, 24H, CHMe<sub>2</sub>), 1.08 (t, free O(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 0.55 (s, 3H, Pd-Me). This material contained 0.5 equiv of Et<sub>2</sub>O per Pd, as determined by <sup>1</sup>H NMR integration.

25

Example 45

[(2,4,6-MePh)<sub>2</sub>DABMe<sub>2</sub>]PdMeCl (0.50 g, 1.05 mmol) was partially dissolved in 40 mL 50/50 methylene chloride/diethylether. To this mixture at room temperature was added AgSbF<sub>6</sub> (0.36 g, 1.05 mmol). The resulting reaction mixture was stirred at room temperature for 45 min. It was then filtered, and the filtrate concentrated in vacuo to afford an oily solid. The latter was washed with diethyl ether and dried to afford the title compound as a beige powder. <sup>1</sup>H NMR (CD<sub>3</sub>CN) δ 6.99 (s, 4H, H<sub>aryl</sub>), 3.38 [q, free O(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>], 2.30-2.00 (overlapping s's, 24H, N=CMe, N=CMe' and aryl Me's), 1.08 (t, free O(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 0.15

35



(s, 3H, Pd-Me). This material contained 0.7 equiv of Et<sub>2</sub>O per Pd, as determined by <sup>1</sup>H MR integration.

Example 46



- 5 A procedure analogous to that used in Example 41, using [(2,6-i-PrPh)<sub>2</sub>DABAn]PdMeCl in place of [(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>]PdMeCl, afforded the title compound in 92% yield. <sup>1</sup>H NMR (CD<sub>3</sub>CN) δ 8.22 (br t, 2H, H<sub>aryl</sub>), 7.60-7.42 (br mult, 8H, H<sub>aryl</sub>), 6.93 (br d, 1H, H<sub>aryl</sub>), 6.53  
10 (br d, 1H, H<sub>aryl</sub>), 3.38 [q, free O(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>], 3.30 (br mult, 4H, CHMe<sub>2</sub>), 1.36 (br d, 6H, CHMe<sub>2</sub>), 1.32 (br d, 6H, CHMe<sub>2</sub>), 1.08 (t, free O(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 1.02 (br d, 6H, CHMe<sub>2</sub>), 0.92 (br d, 6H, CHMe<sub>2</sub>), 0.68 (s, 3H, Pd-Me). The amount of ether contained in the product could not  
15 be determined precisely by <sup>1</sup>H NMR integration, due to overlapping resonances.

Example 47

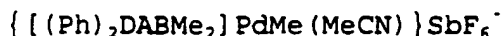


- 20 A procedure analogous to that used in Example 41, using AgOSO<sub>2</sub>CF<sub>3</sub> in place of AgSbF<sub>6</sub>, afforded the title compound as a yellow-orange powder. <sup>1</sup>H NMR in CD<sub>3</sub>CN was identical to that of the title compound of Example 41, but without free ether resonances.

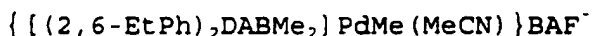
Example 48

- 25  $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdMe}(\text{MeCN})\}\text{SbF}_6^-$   
[(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>]PdMeCl (0.40 g, 0.71 mmol) was dissolved in 15 mL acetonitrile to give an orange solution. To this was added AgSbF<sub>6</sub> (0.25 g, 0.71 mmol) at room temperature. AgCl immediately precipitated  
30 from the resulting bright yellow reaction mixture. The mixture was stirred at room temperature for 3 h. It was then filtered and the AgCl precipitate extracted with 5 mL of acetonitrile. The combined filtrate and extract were concentrated to dryness affording a yellow  
35 solid. This was recrystallized from methylene chloride/petroleum ether affording 0.43 g of the title compound as a bright yellow powder (Yield = 75%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.35-7.24 (mult, 6H, H<sub>aryl</sub>), 2.91 (mult,

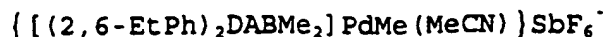
4H, CHMe<sub>2</sub>), 2.29 (s, 3H, N=CMe), 2.28 (s, 3H, N=CMe'),  
 1.81 (s, 3H, N≡CMe), 1.37-1.19 (overlapping d's, 24H,  
 CHMe's), 0.40 (s, 3H, Pd-Me). This compound can also  
 be prepared by addition of acetonitrile to {[(2,6-i-  
 5 PrPh)<sub>2</sub>DABMe<sub>2</sub>]PdMe(Et<sub>2</sub>O)}SbF<sub>6</sub><sup>-</sup>.

Example 49

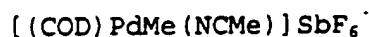
A procedure analogous to that used in Example 48,  
 using [(Ph)<sub>2</sub>DABMe<sub>2</sub>]PdMeCl in place of [(2,6-i-  
 10 PrPh)<sub>2</sub>DABMe<sub>2</sub>]PdMeCl, afforded the title compound as a  
 yellow microcrystalline solid upon recrystallization  
 from methylene chloride / petroleum ether. This  
 complex crystallizes as the acetonitrile solvate from  
 acetonitrile solution at -40°C. <sup>1</sup>H NMR of material  
 15 recrystallized from methylene chloride/petroleum ether:  
 (CDCl<sub>3</sub>) δ 7.46 (mult, 4H, H<sub>aryl</sub>), 7.30 (t, 2H, H<sub>aryl</sub>),  
 7.12 (d, 2H, H<sub>aryl</sub>), 7.00 (d, 2H, H<sub>aryl</sub>), 2.31 (s, 3H,  
 N=CMe), 2.25 (s, 3H, N=CMe'), 1.93 (s, 3H, N≡CMe), 0.43  
 (s, 3H, Pd-Me).

Example 50

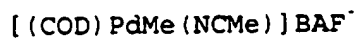
[(2,6-EtPh)<sub>2</sub>DABMe<sub>2</sub>]PdMeCl (0.200 g, 0.396 mmol)  
 was dissolved in 10 mL of acetonitrile to give an  
 orange solution. To this was added NaBAF (0.350 g,  
 25 0.396 mmol). The reaction mixture turned bright yellow  
 and NaCl precipitated. The reaction mixture was  
 stirred at room temperature for 30 min and then  
 filtered through a Celite<sup>®</sup> pad. The Celite<sup>®</sup> pad was  
 extracted with 5 mL of acetonitrile. The combined  
 30 filtrate and extract was concentrated in vacuo to  
 afford an orange solid, recrystallization of which from  
 methylene chloride / petroleum ether at -40°C afforded  
 0.403 g of the title compound as orange crystals (Yield  
 = 74%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.68 (s, 8H, H<sub>ortho</sub> of anion),  
 7.51 (s, 4H, H<sub>para</sub> of anion), 7.33-7.19 (mult, 6H, H<sub>aryl</sub>  
 35 of cation), 2.56-2.33 (mult, 8H, CH<sub>2</sub>CH<sub>3</sub>), 2.11 (s, 3H,  
 N=CMe), 2.09 (s, 3H, N=CMe'), 1.71 (s, 3H, N≡CMe),  
 1.27-1.22 (mult, 12H, CH<sub>2</sub>CH<sub>3</sub>), 0.41 (s, 3H, Pd-Me).

Example 51

A procedure analogous to that used in Example 50, using  $\text{AgSbF}_6$  in place of  $\text{NaBAF}$ , afforded the title compound as yellow crystals in 99% yield after recrystallization from methylene chloride/petroleum ether at  $-40^\circ\text{C}$ .

Example 52

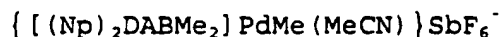
To  $(\text{COD})\text{PdMeCl}$  (1.25 g, 4.70 mmol) was added a solution of acetonitrile (1.93 g, 47.0 mmol) in 20 mL methylene chloride. To this clear solution was added  $\text{AgSbF}_6$  (1.62 g, 4.70 mmol). A white solid immediately precipitated. The reaction mixture was stirred at room temperature for 45 min, and then filtered. The yellow filtrate was concentrated to dryness, affording a yellow solid. This was washed with ether and dried, affording 2.27 g of  $[(\text{COD})\text{PdMe}(\text{NCMe})]\text{SbF}_6^-$  as a light yellow powder (yield = 95%).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  5.84 (mult, 2H,  $\text{CH}=\text{CH}$ ), 5.42 (mult, 2H,  $\text{CH}'=\text{CH}'$ ), 2.65 (mult, 4H,  $\text{CHH}'$ ), 2.51 (mult, 4H,  $\text{CHH}'$ ), 2.37 (s, 3H,  $\text{NCMe}$ ), 1.18 (s, 3H,  $\text{Pd-Me}$ ).

Example 53

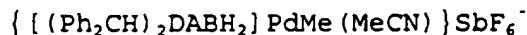
A procedure analogous to that used in Example 52, using  $\text{NaBAF}$  in place of  $\text{AgSbF}_6$ , afforded the title compound as a light beige powder in 96% yield.

Example 54

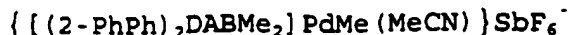
- To a suspension of (2-*t*-BuPh)<sub>2</sub>DABMe<sub>2</sub> (0.138 g, 0.395 mmol) in 10 mL of acetonitrile was added
- 5 [(COD)PdMe(NCMe)]SbF<sub>6</sub> (0.200 g, 0.395 mmol). The resulting yellow solution was stirred at room temperature for 5 min. It was then extracted with 3 x 10 mL of petroleum ether. The yellow acetonitrile phase was concentrated to dryness, affording a bright
- 10 yellow powder. Recrystallization from methylene chloride/petroleum ether at -40 °C afforded 180 mg of the title product as a bright yellow powder (yield = 61%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 7.57 (dd, 2H, H<sub>aryl</sub>), 7.32 (mult, 4H, H<sub>aryl</sub>), 6.88 (dd, 2H, H<sub>aryl</sub>), 6.78 (dd, 2H, H<sub>aryl</sub>), 2.28 (s, 3H, N=CMe), 2.22 (s, 3H, N=CMe'), 1.78
- 15 (s, 3H, N≡CMe), 1.48 (s, 18H, <sup>*t*</sup>Bu), 0.52 (s, 3H, Pd-Me).

Example 55

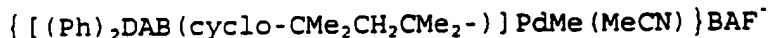
- 20 A procedure analogous to that used in Example 54, using (Np)<sub>2</sub>DABMe<sub>2</sub> in place of (2-*t*-BuPh)<sub>2</sub>DABMe<sub>2</sub>, afforded the title compound as an orange powder in 52% yield after two recrystallizations from methylene chloride/petroleum ether. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 8.20-7.19
- 25 (mult, 14 H, H<sub>aromatic</sub>), 2.36 (d, J = 4.3 Hz, 3H, N=CMe), 2.22 (d, J = 1.4 Hz, 3H, N=CMe'), 1.32 (s, 3H, NCMe), 0.22 (s, 3H, Pd-Me).

Example 56

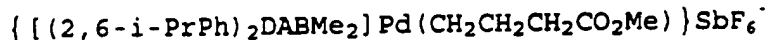
- 30 A procedure analogous to that used in Example 54, using (Ph<sub>2</sub>CH)<sub>2</sub>DABH<sub>2</sub> in place of (2-*t*-BuPh)<sub>2</sub>DABMe<sub>2</sub>, afforded the title compound as a yellow microcrystalline solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.69 (s, 1H, N=CH), 7.65 (s, 1H, N=CH'), 7.44-7.08 (mult, 20H, H<sub>aryl</sub>), 6.35 (2, 2H, CHPh<sub>2</sub>), 1.89 (s, 3H, NCMe), 0.78
- 35 (s, 3H, Pd-Me).

Example 57

A procedure analogous to that used in Example 54, using (2-PhPh)<sub>2</sub>DABMe<sub>2</sub> in place of (2-t-BuPh)<sub>2</sub>DABMe<sub>2</sub>,  
 5 afforded the title compound as a yellow-orange powder in 90% yield. Two isomers, due to cis or trans orientations of the two ortho phenyl groups on either side of the square plane, were observed by <sup>1</sup>H NMR. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 7.80-6.82 (mult, 18H, H<sub>aryl</sub>), 1.98, 1.96,  
 10 1.90, 1.83, 1.77, 1.73 (singlets, 9H, N=CMe, N=CMe', NCMe for cis and trans isomers), 0.63, 0.61 (singlets, 3H, Pd-Me for cis and trans isomers).

Example 58

15 To a solution of [(COD)PdMe(NCMe)]BAF<sup>-</sup> (0.305 g, 0.269 mmol) dissolved in 15 mL of acetonitrile was added N,N'-diphenyl-2,2',4,4'-tetramethyl-cyclopentylidiazine (0.082 g, 0.269 mmol). A gold colored solution formed rapidly and was stirred at room  
 20 temperature for 20 min. The solution was then extracted with 4 x 5 mL petroleum ether, and the acetonitrile phase concentrated to dryness to afford a yellow powder. This was recrystallized from methylene chloride/petroleum ether at -40°C to afford 0.323 g  
 25 (90%) of the title compound as a yellow-orange, crystalline solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.71 (s, 8H, H<sub>ortho</sub> of anion), 7.54 (s, 4H, H<sub>para</sub> of anion), 7.45-6.95 (mult, 10H, H<sub>aryl</sub> of cation), 1.99 (s, 2H, CH<sub>2</sub>), 1.73 (s, 3H, NCMe), 1.15 (s, 6H, Me<sub>2</sub>), 1.09 (s, 6H, Me'<sub>2</sub>),  
 30 0.48 (s, 3H, Pd-Me).

Example 59

Under a nitrogen atmosphere {[(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>]PdMe(Et<sub>2</sub>O)}SbF<sub>6</sub><sup>-</sup> (3.60 g, 4.30 mmol) was  
 35 weighed into a round bottom flask containing a magnetic stirbar. To this was added a -40°C solution of methyl acrylate (1.85 g, 21.5 mmol) dissolved in 100 ml of methylene chloride. The resulting orange solution was

stirred for 10 min, while being allowed to warm to room temperature. The reaction mixture was then concentrated to dryness, affording a yellow-brown solid. The crude product was extracted with methylene chloride, and the orange-red extract concentrated, layered with an equal volume of petroleum ether, and cooled to  $-40^{\circ}\text{C}$ . This afforded 1.92 g of the title compound as yellow-orange crystals. An additional 1.39 g was obtained as a second crop from the mother liquor; total yield = 91%.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  7.39-7.27 (mult, 6H,  $\text{H}_{\text{aryl}}$ ), 3.02 (s, 3H, OMe), 2.97 (sept, 4H,  $\text{CHMe}_2$ ), 2.40 (mult, 2H,  $\text{CH}_2$ ), 2.24 (s, 3H,  $\text{N}=\text{CMe}$ ), 2.22 (s, 3H,  $\text{N}=\text{CMe}'$ ), 1.40-1.20 (mult, 26H,  $\text{CHMe}_2$  and  $\text{CH}_2'$ ), 0.64 (mult, 2H,  $\text{CH}_2''$ ).

15

Example 60

$\{[(2,6\text{-i-PrPh})_2\text{DABH}_2]\text{Pd}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{Me})\}\text{SbF}_6^-$   
 $\text{AgSbF}_6$  (0.168 g, 0.489 mmol) was added to a  $-40^{\circ}\text{C}$  solution of  $\{[(2,6\text{-i-PrPh})_2\text{DABH}_2]\text{PdMeCl}$  (0.260 g, 0.487 mmol) and methyl acrylate (0.210 g, 2.44 mmol) in 10 mL methylene chloride. The reaction mixture was stirred for 1 h while warming to room temperature, and then filtered. The filtrate was concentrated in vacuo to give a saturated solution of the title compound, which was then layered with an equal volume of petroleum ether and cooled to  $-40^{\circ}\text{C}$ . Red-orange crystals precipitated from the solution. These were separated by filtration and dried, affording 0.271 g of the title compound (68% yield).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  8.38 (s, 1H,  $\text{N}=\text{CH}$ ), 8.31 (s, 1H,  $\text{N}=\text{CH}'$ ), 7.41-7.24 (mult, 6H,  $\text{H}_{\text{aryl}}$ ), 3.16 (mult, 7H, OMe and  $\text{CHMe}_2$ ), 2.48 (mult, 2H,  $\text{CH}_2$ ), 1.65 (t, 2H,  $\text{CH}_2'$ ), 1.40-1.20 (mult, 24H,  $\text{CHMe}_2$ ), 0.72 (mult, 2H,  $\text{CH}_2''$ ).

35

Example 61

$\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{Pd}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{Me})\}[\text{B}(\text{C}_6\text{F}_5)_3\text{Cl}]$   
 $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdMeCl}$  (0.038 g, 0.067 mmol) and methyl acrylate (0.028 g, 0.33 mmol) were dissolved in  $\text{CD}_2\text{Cl}_2$ . To this solution was added  $\text{B}(\text{C}_6\text{F}_5)_3$  (0.036

g, 0.070 mmol).  $^1\text{H}$  NMR of the resulting reaction mixture showed formation of the title compound.

#### Example 62

A 100 mL autoclave was charged with chloroform (50 mL),  $\{[(2\text{-}t\text{-BuPh})_2\text{DABMe}_2]\text{PdMe}(\text{NCMe})\}\text{SbF}_6^-$  (0.090 g, 0.12 mmol), and ethylene (2.1 MPa). The reaction mixture was stirred at  $25^\circ\text{C}$  and 2.1 MPa ethylene for 3 h. The ethylene pressure was then vented and volatiles removed from the reaction mixture in vacuo to afford 2.695 g of branched polyethylene. The number average molecular weight ( $M_n$ ), calculated by  $^1\text{H}$  NMR integration of aliphatic vs. olefinic resonances, was 1600. The degree of polymerization, DP, was calculated on the basis of the  $^1\text{H}$  NMR spectrum to be 59; for a linear polymer this would result in 18 methyl-ended branches per 1000 methylenes. However, based on the  $^1\text{H}$  NMR spectrum the number of methyl-ended branches per 1000 methylenes was calculated to be 154. Therefore, it may be concluded that this material was branched polyethylene.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.38 (mult, vinyl H's), 1.95 (mult, allylic methylenes), 1.62 (mult, allylic methyls), 1.24 (mult, non-allylic methylenes and methines), 0.85 (mult, non-allylic methyls).

#### Example 63

A suspension of  $\{[(2\text{-}t\text{-BuPh})_2\text{DABMe}_2]\text{PdMe}(\text{NCMe})\}\text{SbF}_6^-$  (0.015 g, 0.02 mmol) in 5 mL FC-75 was agitated under 2.8 MPa of ethylene for 30 min. The pressure was then increased to 4.1 MPa and maintained at this pressure for 3 h. During this time the reaction temperature varied between  $25$  and  $40^\circ\text{C}$ . A viscous oil was isolated from the reaction mixture by decanting off the FC-75 and dried in vacuo. The number average molecular weight ( $M_n$ ), calculated by  $^1\text{H}$  NMR integration of aliphatic vs. olefinic resonances, was 2600. DP for this material was calculated on the basis of the  $^1\text{H}$  NMR spectrum to be 95; for a linear polymer this would result in 11 methyl-ended branches per 1000 methylenes. However, based on the  $^1\text{H}$  NMR

spectrum the number of methyl-ended branches per 1000 methylenes was calculated to be 177.

Example 64

A 100 mL autoclave was charged with chloroform (55 mL),  $\{[(2\text{-PhPh})_2\text{DABMe}_2]\text{PdMe}(\text{NCMe})\}\text{SbF}_6^-$  (0.094 g, 0.12 mmol), and ethylene (2.1 MPa). The reaction mixture was stirred at 25°C and 2.1 MPa ethylene for 3 h. The ethylene pressure was then vented and volatiles removed from the reaction mixture in vacuo to afford 2.27 g of a pale yellow oil. Mn was calculated on the basis of  $^1\text{H}$  NMR integration of aliphatic vs. olefinic resonances to be 200. The degree of polymerization, DP, was calculated on the basis of the  $^1\text{H}$  NMR spectrum to be 7.2; for a linear polymer this would result in 200 methyl-ended branches per 1000 methylenes. However, based on the  $^1\text{H}$  NMR spectrum the number of methyl-ended branches per 1000 methylenes was calculated to be 283.

Example 65

A suspension of  $\{[(2\text{-PhPh})_2\text{DABMe}_2]\text{PdMe}(\text{NCMe})\}\text{SbF}_6^-$  (0.016 g, 0.02 mmol) in 5 mL FC-75 was agitated under 1.4 MPa of ethylene for 3 h 40 min. During this time the reaction temperature varied between 23 and 41°C. A viscous oil (329 mg) was isolated from the reaction mixture by decanting off the FC-75 and dried in vacuo. Mn was calculated on the basis of  $^1\text{H}$  NMR integration of aliphatic vs. olefinic resonances to be 700. The degree of polymerization, DP, was calculated on the basis of the  $^1\text{H}$  NMR spectrum to be 24.1; for a linear polymer this would result in 45 methyl-ended branches per 1000 methylenes. However, based on the  $^1\text{H}$  NMR spectrum the number of methyl-ended branches per 1000 methylenes was calculated to be 173.

Example 66

A 100 mL autoclave was charged with FC-75 (50 mL),  $\{(\text{Ph}_2\text{DABMe}_2)\text{PdMe}(\text{NCMe})\}\text{SbF}_6^-$  (0.076 g, 0.12 mmol) and ethylene (2.1 MPa). The reaction mixture was stirred at 24°C for 1.5 h. The ethylene pressure was then vented, and the FC-75 mixture removed from the reactor.



A small amount of insoluble oil was isolated from the mixture by decanting off the FC-75. The reactor was washed out with 2 x 50 mL  $\text{CHCl}_3$ , and the washings added to the oil. Volatiles removed from the resulting solution in vacuo to afford 144 mg of an oily solid. Mn was calculated on the basis of  $^1\text{H}$  NMR integration of aliphatic vs. olefinic resonances to be 400. The degree of polymerization, DP, was calculated on the basis of the  $^1\text{H}$  NMR spectrum to be 13.8; for a linear polymer this would result in 83 methyl-ended branches per 1000 methylenes. However, based on the  $^1\text{H}$  NMR spectrum the number of methyl-ended branches per 1000 methylenes was calculated to be 288.

#### Example 67

A 100 mL autoclave was charged with chloroform (50 mL),  $\{[(2,6\text{-EtPh})_2\text{DABMe}_2]\text{PdMe}(\text{NCMe})\}\text{BAF}^-$  (0.165 g, 0.12 mmol), and ethylene (2.1 MPa). The reaction mixture was stirred under 2.1 MPa of ethylene for 60 min; during this time the temperature inside the reactor increased from 22 to 48°C. The ethylene pressure was then vented and volatiles removed from the reaction mixture in vacuo to afford 15.95 g of a viscous oil.  $^1\text{H}$  NMR of this material showed it to be branched polyethylene with 135 methyl-ended branches per 1000 methylenes. GPC analysis in trichlorobenzene (vs. a linear polyethylene standard) gave  $M_n = 10,400$ ,  $M_w = 22,100$ .

#### Example 68

This was run identically to Example 67, but with  $\{[(2,6\text{-EtPh})_2\text{DABMe}_2]\text{PdMe}(\text{NCMe})\}\text{SbF}_6^-$  (0.090 g, 0.12 mmol) in place of the corresponding BAF salt. The temperature of the reaction increased from 23 to 30°C during the course of the reaction. 5.25 g of a viscous oil was isolated,  $^1\text{H}$  NMR of which showed it to be branched polyethylene with 119 methyl-ended branches per 1000 methylenes.

Example 69

A suspension of  $\{[(\text{Np})_2\text{DABMe}_2]\text{PdMe}(\text{NCMe})\}\text{SbF}_6^-$  (0.027 g, 0.02 mmol) in 5 mL FC-75 was agitated under 1.4 MPa of ethylene for 3 h; during this time the temperature inside the reactor varied between 25 and 40°C. Two FC-75 insoluble fractions were isolated from the reaction mixture. One fraction, a non-viscous oil floating on top of the FC-75, was removed by pipette and shown by  $^1\text{H}$  NMR to be branched ethylene oligomers for which  $M_n = 150$  and with 504 methyl-ended branches per 1000 methylenes. The other fraction was a viscous oil isolated by removing FC-75 by pipette; it was shown by  $^1\text{H}$  NMR to be polyethylene for which  $M_n = 650$  and with 240 methyl-ended branches per 1000 methylenes.

Example 70

A suspension of  $\{[(\text{Ph}_2\text{CH})_2\text{DABH}_2]\text{PdMe}(\text{NCMe})\}\text{SbF}_6^-$  (0.016 g, 0.02 mmol) in 5 mL FC-75 was agitated under 1.4 MPa of ethylene for 3 h 40 min. During this time the reaction temperature varied between 23 and 41°C. A viscous oil (43 mg) was isolated from the reaction mixture by decanting off the FC-75 and dried in vacuo.  $M_n$  was calculated on the basis of  $^1\text{H}$  NMR integration of aliphatic vs. olefinic resonances to be approximately 2000. The degree of polymerization, DP, was calculated on the basis of the  $^1\text{H}$  NMR spectrum to be 73; for a linear polymer this would result in 14 methyl-ended branches per 1000 methylenes. However, based on the  $^1\text{H}$  NMR spectrum the number of methyl-ended branches per 1000 methylenes was calculated to be 377.

Example 71

A 100 mL autoclave was charged with FC-75 (50 mL),  $\{(\text{Ph}_2\text{DAB}(\text{cyclo}-\text{CMe}_2\text{CH}_2\text{CMe}_2-))\text{PdMe}(\text{MeCN})\}\text{BAF}^-$  (0.160 g, 0.12 mmol) and ethylene (2.1 MPa). The reaction mixture was stirred at 24-25°C for 3.5 h. The ethylene pressure was then vented, and the cloudy FC-75 mixture removed from the reactor. The FC-75 mixture was extracted with chloroform, and the chloroform extract concentrated to dryness affording 0.98 g of an oil.  $M_n$

was calculated on the basis of  $^1\text{H}$  NMR integration of aliphatic vs. olefinic resonances to be 500. The degree of polymerization, DP, was calculated on the basis of the  $^1\text{H}$  NMR spectrum to be 19.5; for a linear polymer this would result in 57 methyl-ended branches per 1000 methylenes. However, based on the  $^1\text{H}$  NMR spectrum the number of methyl-ended branches per 1000 methylenes was calculated to be 452.

#### Example 72

10 A 100 mL autoclave was charged with FC-75 (50 mL),  $\{[(4\text{-NMe}_2\text{Ph})_2\text{DABMe}_2]\text{PdMe}(\text{MeCN})\}\text{SbF}_6^- (\text{MeCN})$  (0.091 g, 0.12 mmol) and ethylene (2.1 MPa). The reaction mixture was stirred at  $24^\circ\text{C}$  for 1.5 h. The ethylene pressure was then vented, and the cloudy FC-75 mixture removed from the reactor. The FC-75 was extracted with 15 3 x 25 mL of chloroform. The reactor was washed out with 3 x 40 mL  $\text{CHCl}_3$ , and the washings added to the extracts. Volatiles removed from the resulting solution in vacuo to afford 556 mg of an oil. Mn was 20 calculated on the basis of  $^1\text{H}$  NMR integration of aliphatic vs. olefinic resonances to be 200. The degree of polymerization, DP, was calculated on the basis of the  $^1\text{H}$  NMR spectrum to be 8.4; for a linear polymer this would result in 154 methyl-ended branches per 1000 methylenes. However, based on the  $^1\text{H}$  NMR 25 spectrum the number of methyl-ended branches per 1000 methylenes was calculated to be 261.

#### Example 73

Under nitrogen, a 250 mL Schlenk flask was charged 30 with 10.0 g of the monomer  $\text{CH}_2=\text{CHCO}_2\text{CH}_2\text{CH}_2(\text{CF}_2)_n\text{CF}_3$  (avg  $n = 9$ ), 40 mL of methylene chloride, and a magnetic stirbar. To the rapidly stirred solution was added  $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdMe}(\text{OEt}_2)\}\text{SbF}_6^-$  (0.075 g, 0.089 mmol) in small portions. The resulting yellow-orange 35 solution was stirred under 1 atm of ethylene for 18 h. The reaction mixture was then concentrated, and the viscous product extracted with ~ 300 mL of petroleum ether. The yellow filtrate was concentrated to

dryness, and extracted a second time with ~ 150 mL petroleum ether. ~ 500 mL of methanol was added to the filtrate; the copolymer precipitated as an oil which adhered to the sides of the flask, and was isolated by  
5 decanting off the petroleum ether/ methanol mixture. The copolymer was dried, affording 1.33 g of a slightly viscous oil. Upon standing for several hours, an additional 0.70 g of copolymer precipitated from the petroleum ether/ methanol mixture. By  $^1\text{H}$  NMR  
10 integration, it was determined that the acrylate content of this material was 4.2 mole%, and that it contained 26 ester and 87 methyl-ended branches per 1000 methylenes. GPC analysis in tetrahydrofuran (vs. a PMMA standard) gave  $M_n = 30,400$ ,  $M_w = 40,200$ .  $^1\text{H}$  NMR  
15 ( $\text{CDCl}_3$ )  $\delta$  4.36 (t,  $\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_2\text{R}_f$ ), 2.45 (mult,  $\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_2\text{R}_f$ ), 2.31 (t,  $\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_2\text{R}_f$ ), 1.62 (mult,  $\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_2\text{R}_f$ ), 1.23 (mult, other methylenes and methines), 0.85 (mult, methyls).  $^{13}\text{C}$  NMR gave branching per 1000  $\text{CH}_2$ : Total methyls (91.3), Methyl  
20 (32.8), Ethyl (20), Propyl (2.2), Butyl (7.7), Amyl (2.2),  $\geq\text{Hex}$  and end of chains (22.1). GPC analysis in THF gave  $M_n = 30,400$ ,  $M_w = 40,200$  vs. PMMA.

#### Example 74

A 100 mL autoclave was charged with  
25  $[\text{Pd}(\text{CH}_3\text{CH}_2\text{CN})_4](\text{BF}_4)_2$  (0.058 g, 0.12 mmol) and chloroform (40 mL). To this was added a solution of (2,6-i-PrPh) $_2\text{DABMe}_2$  (0.070 g, 0.17 mmol) dissolved in 10 mL of chloroform under ethylene pressure (2.1 MPa). The pressure was maintained at 2.1 MPa for 1.5 h,  
30 during which time the temperature inside the reactor increased from 22 to 35°C. The ethylene pressure was then vented and the reaction mixture removed from the reactor. The reactor was washed with 3 x 50 mL of chloroform, the washings added to the reaction mixture,  
35 and volatiles removed from the resulting solution in vacuo to afford 9.77 g of a viscous oil.  $^1\text{H}$  NMR of this material showed it to be branched polyethylene with 96 methyl-ended branches per 1000 methylenes.

Example 75

A 100 mL autoclave was charged with  
[Pd(CH<sub>3</sub>CN)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub> (0.053 g, 0.12 mmol) and chloroform  
(50 mL). To this was added a solution of (2,6-i-  
5 PrPh)<sub>2</sub>DABMe<sub>2</sub> (0.070 g, 0.17 mmol) dissolved in 10 mL of  
chloroform under ethylene pressure (2.1 MPa). The  
pressure was maintained at 2.1 MPa for 3.0 h, during  
which time the temperature inside the reactor increased  
from 23 to 52°C. The ethylene pressure was then vented  
10 and the reaction mixture removed from the reactor. The  
reactor was washed with 3 x 50 mL of chloroform, the  
washings added to the reaction mixture, and volatiles  
removed from the resulting solution in vacuo to afford  
25.98 g of a viscous oil. <sup>1</sup>H NMR of this material  
15 showed it to be branched polyethylene with 103 methyl-  
ended branches per 1000 methylenes. GPC analysis in  
trichlorobenzene gave M<sub>n</sub> = 10,800, M<sub>w</sub> = 21,200 vs.  
linear polyethylene.

Example 76

20 A mixture of 20 mg (0.034 mmol) of [(2,6-i-  
PrPh)<sub>2</sub>DABH<sub>2</sub>]NiBr<sub>2</sub> and 60 mL dry, deaerated toluene was  
magnetically-stirred under nitrogen in a 200-mL three-  
necked flask with a gas inlet tube, a thermometer, and  
a gas exit tube which vented through a mineral oil  
25 bubbler. To this mixture, 0.75 mL (65 eq) of 3M  
poly(methylalumoxane) (PMAO) in toluene was added via  
syringe. The resulting deep blue-black catalyst  
solution was stirred as ethylene was bubbled through at  
about 5 ml and 1 atm for 2 hr. The temperature of the  
30 mixture rose to 60°C in the first 15 min and then  
dropped to room temperature over the course of the  
reaction.

The product solution was worked up by blending  
with methanol; the resulting white polymer was washed  
35 with 2N HCl, water, and methanol to yield after drying  
(50°C/vacuum/nitrogen purge) 5.69g (6000 catalyst  
turnovers) of polyethylene which was easily-soluble in  
hot chlorobenzene. Differential scanning calorimetry

exhibited a broad melting point at 107°C (67 J/g). Gel permeation chromatography (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal calibration theory):  
5  $M_n=22,300$ ;  $M_w=102,000$ ;  $M_w/M_n=4.56$ .  $^{13}\text{C}$  NMR analysis: branching per 1000  $\text{CH}_2$ : total Methyls (60), Methyl (41), Ethyl (5.8), Propyl (2.5), Butyl (2.4), Amyl (1.2),  $\geq$ Hexyl and end of chain (5); chemical shifts were referenced to the solvent: the high field carbon  
10 of 1,2,4-trichlorobenzene (127.8 ppm). A film of polymer (pressed at 200°C) was strong and could be stretched and drawn without elastic recovery.

#### Example 77

In a Parr<sup>®</sup> 600-mL stirred autoclave under  
15 nitrogen was combined 23 mg (0.039 mmol) of [(2,6-i-PrPh)DABH<sub>2</sub>]NiBr<sub>2</sub>, 60 mL of dry toluene, and 0.75 mL of poly(methylalumoxane) at 28°C. The mixture was stirred, flushed with ethylene, and pressurized to 414 kPa with ethylene. The reaction was stirred at 414 kPa  
20 for 1 hr; the internal temperature rose to 31°C over this time. After 1 hr, the ethylene was vented and 200 mL of methanol was added with stirring to the autoclave. The resulting polymer slurry was filtered; the polymer adhering to the autoclave walls and  
25 impeller was scraped off and added to the filtered polymer. The product was washed with methanol and acetone and dried (80°C/vacuum/nitrogen purge) to yield 5.10g (4700 catalyst turnovers) of polyethylene. Differential scanning calorimetry exhibited a melting  
30 point at 127°C (170 J/g). Gel permeation chromatography (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal calibration theory):  $M_n=49,300$ ;  $M_w=123,000$ ;  $M_w/M_n=2.51$ . Intrinsic viscosity (trichlorobenzene,  
35 135°C): 1.925 dL/g. Absolute molecular weight averages corrected for branching:  $M_n=47,400$ ;  $M_w=134,000$ ;  $M_w/M_n=2.83$ .  $^{13}\text{C}$  NMR analysis; branching per 1000  $\text{CH}_2$ : total Methyls (10.5), Methyl (8.4), Ethyl (0.9), Propyl

(0), Butyl (0),  $\geq$ Butyl and end of chain (1.1); chemical shifts were referenced to the solvent: the high field carbon of 1,2,4-trichlorobenzene (127.8 ppm). A film of polymer (pressed at 200°C) was strong and stiff and could be stretched and drawn without elastic recovery. This polyethylene is much more crystalline and linear than the polymer of Example 76. This example shows that only a modest pressure increase from 1 atm to 414 kPa allows propagation to successfully compete with rearrangement and isomerization of the polymer chain by this catalyst, thus giving a less-branched, more-crystalline polyethylene.

#### Example 78

A mixture of 12 mg (0.020 mmol) of [(2,6-i-PrPh)DABH<sub>2</sub>]NiBr<sub>2</sub> and 40 mL dry, deaerated toluene was magnetically-stirred under nitrogen at 15°C in a 100-mL three-necked flask with an addition funnel, a thermometer, and a nitrogen inlet tube which vented through a mineral oil bubbler. To this mixture, 0.5 mL of poly(methylalumoxane) in toluene was added via syringe; the resulting burgundy catalyst solution was stirred for 5 min and allowed to warm to room temperature. Into the addition funnel was condensed (via a Dry Ice condenser on the top of the funnel) 15 mL (about 10g) of cis-2-butene. The catalyst solution was stirred as the cis-2-butene was added as a liquid all at once, and the mixture was stirred for 16 hr. The product solution was treated with 1 mL of methanol and was filtered through diatomaceous earth; rotary evaporation yielded 0.35g (300 catalyst turnovers) of a light yellow grease, poly-2-butene. <sup>13</sup>C NMR analysis; branching per 1000 CH<sub>2</sub>: total Methyls (365), Methyl (285), Ethyl (72),  $\geq$ Butyl and end of chain (8); chemical shifts were referenced to the solvent chloroform-d<sub>1</sub> (77 ppm).

Listed below are the <sup>13</sup>C NMR data upon which the above analysis is based.

<sup>13</sup>C NMR DataCDCl<sub>3</sub>, RT, 0.05M CnAcAc

Freq ppm	Intensity	
41.6071	11.2954	
41.1471	13.7193	
38.6816	3.55568	
37.1805	7.07882	
36.8657	33.8859	
36.7366	35.1101	
36.6196	33.8905	
36.2645	12.1006	
35.9094	13.3271	
35.8004	11.8845	
35.5785	4.20104	
34.7351	24.9682	
34.4325	39.3436	
34.3114	59.2878	
34.1177	125.698	
33.9886	121.887	
33.8837	120.233	
33.5326	49.8058	
33.004	132.842	
32.7377	51.2221	
32.657	55.6128	
32.3705	18.1589	
31.5876	9.27643	
31.3818	16.409	
31.0066	15.1861	
30.0946	41.098	
29.9736	42.8009	
29.7072	106.314	
29.3602	60.0884	
29.2512	35.0694	
29.114	26.6437	
28.9769	29.1226	
27.9358	3.57351	
27.7501	3.56527	
27.0682	14.6121	
26.7333	81.0769	
26.3257	14.4591	
26.015	11.8399	
25.3008	8.17451	
25.0627	5.98833	
22.4801	3.60955	2B <sub>4</sub>
22.3308	10.4951	2B <sub>5</sub> +, EOC
19.6192	90.3272	1B <sub>1</sub>
19.4618	154.354	1B <sub>1</sub>
19.3085	102.085	1B <sub>1</sub>
18.9937	34.7667	1B <sub>1</sub>
18.8525	38.7651	1B <sub>1</sub>
13.7721	11.2148	1B <sub>4</sub> +, EOC, 1B <sub>3</sub>
11.0484	54.8771	1B <sub>2</sub>
10.4552	10.8437	1B <sub>2</sub>
10.1283	11.0735	1B <sub>2</sub>
9.99921	9.36226	1B <sub>2</sub>



Example 79

A mixture of 10 mg (0.017 mmol) of [(2,6-i-PrPh)DABH<sub>2</sub>]NiBr<sub>2</sub> and 40 mL dry, deaerated toluene was magnetically-stirred under nitrogen at 5°C in a 100-mL three-necked flask with an addition funnel, a thermometer, and a nitrogen inlet tube which vented through a mineral oil bubbler. To this mixture, 0.5 mL of 3M poly(methylalumoxane) in toluene was added via syringe; the resulting burgundy catalyst solution was stirred at 5°C for 40 min. Into the addition funnel was condensed (via a Dry Ice condenser on the top of the funnel) 20 mL (about 15 g) of 1-butene. The catalyst solution was stirred as the 1-butene was added as a liquid all at once. The reaction temperature rose to 50°C over 30 min and then dropped to room temperature as the mixture was stirred for 4 hr. The product solution was treated with 1 mL of methanol and was filtered through diatomaceous earth; rotary evaporation yielded 6.17 g (1640 catalyst turnovers) of clear, tacky poly-1-butene rubber. Gel permeation chromatography (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal calibration theory):  $M_n=64,700$ ;  $M_w=115,000$ ;  $M_w/M_n=1.77$ . <sup>13</sup>C NMR analysis; branching per 1000 CH<sub>2</sub>: total Methyls (399), Methyl (86), Ethyl (272), ≥Butyl and end of chain (41); chemical shifts were referenced to the solvent chloroform-d<sub>1</sub> (77 ppm). This example demonstrates the polymerization of an alpha-olefin and shows the differences in branching between a polymer derived from a 1-olefin (this example) and a polymer derived from a 2-olefin (Example 78). This difference shows that the internal olefin of Example 78 is not first isomerized to an alpha-olefin before polymerizing; thus this catalyst is truly able to polymerize internal olefins.

Listed below are the <sup>13</sup>C NMR data upon which the above analysis is based.

<sup>13</sup> C NMR Data		
CDCl <sub>3</sub> , RT, 0.05M CrAcAc		
Freq ppm	Intensity	
43.8708	6.42901	
41.5304	11.1597	
41.0825	16.1036	
38.7623	103.647	
38.1247	50.3288	
37.3338	24.6017	
36.8173	30.0925	
35.756	55.378	
35.0337	22.3563	
34.1419	64.8431	
33.8514	55.3508	
33.4116	90.2438	
33.0645	154.939	
32.7094	51.3245	
32.431	23.0013	3B <sub>5</sub>
30.946	12.8866	3B <sub>6</sub> +
30.1551	26.1216	
29.7516	54.6262	
29.4248	40.7879	
27.6008	8.64277	
27.2417	20.1564	
27.1207	21.9735	
26.7777	45.0824	
26.0755	66.0697	
25.6599	77.1097	
24.3807	8.9175	
23.4809	32.0249	2B <sub>4</sub> , 2B <sub>5</sub> +, 2EOC
22.8393	8.06774	
22.1372	16.4732	
19.4981	57.7003	1B <sub>1</sub>
19.3609	70.588	1B <sub>1</sub>
15.132	17.2402	1B <sub>4</sub> +
13.8448	7.9343	1B <sub>4</sub> +
12.2509	27.8653	
12.037	27.0118	
11.0766	6.61931	1B <sub>2</sub>
10.2938	98.0101	1B <sub>2</sub>
10.1364	104.811	1B <sub>2</sub>

Example 80

- 5 A 22-mg (0.037-mmol) sample of [(2,6-i-PrPh)DABH<sub>2</sub>]NiBr<sub>2</sub> was introduced into a 600-mL stirred Parr® autoclave under nitrogen. The autoclave was sealed and 75 mL of dry, deaerated toluene was introduced into the autoclave via gas tight syringe
- 10 through a port on the autoclave head. Then 0.6 mL of 3M poly(methylalumoxane) was added via syringe and stirring was begun. The autoclave was pressurized with

propylene to 414 kPa and stirred with continuous propylene feed. There was no external cooling. The internal temperature quickly rose to 33°C upon initial propylene addition but gradually dropped back to 24°C over the course of the polymerization. After about 7 min, the propylene feed was shut off and stirring was continued; over a total polymerization time of 1.1 hr, the pressure dropped from 448 kPa to 358 kPa. The propylene was vented and the product, a thin, honey-colored solution, was rotary evaporated to yield 1.65g of a very thick, brown semi-solid. This was dissolved in chloroform and filtered through diatomaceous earth; concentration yielded 1.3 g (835 catalyst turnovers) of tacky, yellow polypropylene rubber. Gel permeation chromatography (trichlorobenzene, 135°C, polystyrene reference, results calculated as polypropylene using universal calibration theory):  $M_n=7,940$ ;  $M_w=93,500$ ;  $M_w/M_n=11.78$ .

#### Example 81

A mixture of 34 mg (0.057 mmol) of [(2,6-i-PrPh)DABH<sub>2</sub>]<sub>2</sub>NiBr<sub>2</sub> and 20 mL dry, deaerated toluene was magnetically-stirred under nitrogen at 5°C in a 100-mL three-necked flask with a thermometer and a nitrogen inlet tube which vented through a mineral oil bubbler. To this mixture, 0.7 mL of 3M poly(methylalumoxane) in toluene was added via syringe and the resulting deep blue-black solution was stirred for 30 min at 5°C. To this catalyst solution was added 35 mL of dry, deaerated cyclopentene, and the mixture was stirred and allowed to warm to room temperature over 23 hr. The blue-black mixture was filtered through alumina to remove dark blue-green solids (oxidized aluminum compounds from PMAO); the filtrate was rotary evaporated to yield 1.2 g (310 catalyst turnovers) of clear liquid cyclopentene oligomers.

#### Example 82

A 20-mg (0.032 mmol) sample of [(2,6-i-PrPh)DABMe<sub>2</sub>]<sub>2</sub>NiBr<sub>2</sub> was placed in Parr® 600-mL stirred

autoclave under nitrogen. The autoclave was sealed and 100 mL of dry, deaerated toluene and 0.6 mL of 3M poly(methylalumoxane) were injected into the autoclave through the head port, and mixture was stirred under  
5 nitrogen at 20°C for 50 min. The autoclave body was immersed in a flowing water bath and the autoclave was then pressurized with ethylene to 2.8 MPa with stirring as the internal temperature rose to 53°C. The autoclave was stirred at 2.8 MPa (continuous ethylene  
10 feed) for 10 min as the temperature dropped to 29°C, and the ethylene was then vented. The mixture stood at 1 atm for 10 min; vacuum was applied to the autoclave for a few minutes and then the autoclave was opened.

The product was a stiff, swollen polymer mass  
15 which was scraped out, cut up, and fed in portions to 500 mL methanol in a blender. The polymer was then boiled with a mixture of methanol (200 mL) and trifluoroacetic acid (10 mL), and finally dried under high vacuum overnight to yield 16.8g (18,700 catalyst  
20 turnovers) of polyethylene. The polymer was somewhat heterogeneous with respect to crystallinity, as can be seen from the differential scanning calorimetry data below; amorphous and crystalline pieces of polymer could be picked out of the product. Crystalline  
25 polyethylene was found in the interior of the polymer mass; amorphous polyethylene was on the outside. The crystalline polyethylene was formed initially when the ethylene had good access to the catalyst; as the polymer formed limited mass transfer, the catalyst  
30 became ethylene-starved and began to make amorphous polymer. Differential scanning calorimetry:  
(crystalline piece of polymer): mp: 130°C (150J/g);  
(amorphous piece of polymer): -48°C (Tg); mp: 42°C (3J/g), 96°C (11J/g). Gel permeation chromatography  
35 (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal calibration theory):  $M_n=163,000$ ;  $M_w=534,000$ ;  $M_w/M_n=3.27$ . This example demonstrates the effect of

ethylene mass transfer on the polymerization and shows that the same catalyst can make both amorphous and crystalline polyethylene. The bulk of the polymer was crystalline: a film pressed at 200°C was tough and stiff.

#### Example 83

A 29-mg (0.047 mmol) sample of [(2,6-i-PrPh)DABMe<sub>2</sub>]NiBr<sub>2</sub> was placed in Parr® 600-mL stirred autoclave under nitrogen. The autoclave was sealed and 10 100 mL of dry, deaerated toluene and 0.85 mL of 3M poly(methylalumoxane) were injected into the autoclave through the head port. The mixture was stirred under nitrogen at 23°C for 30 min. The autoclave body was immersed in a flowing water bath and the autoclave was 15 pressurized with ethylene to 620 kPa with stirring. The internal temperature peaked at 38°C within 2 min. The autoclave was stirred at 620 kPa (continuous ethylene feed) for 5 min as the temperature dropped to 32°C. The ethylene was then vented, the regulator was 20 readjusted, and the autoclave was pressurized to 34.5 kPa (gauge) and stirred for 20 min (continuous ethylene feed) as the internal temperature dropped to 22°C. In the middle of this 20 min period, the ethylene feed was temporarily shut off for 1 min, during which time the 25 autoclave pressure dropped from 34.5 kPa (gauge) to 13.8 kPa; the pressure was then restored to 34.5 kPa. After stirring 20 min at 34.5 kPa, the autoclave was once again pressurized to 620 kPa for 5 min; the internal temperature rose from 22°C to 34°C. The 30 ethylene feed was shut off for about 30 sec before venting; the autoclave pressure dropped to about 586 kPa.

The ethylene was vented; the product was a dark, thick liquid. Methanol (200 mL) was added to the 35 autoclave and the mixture was stirred for 2 hr. The polymer, swollen with toluene, had balled up on the stirrer, and the walls and bottom of the autoclave were coated with white, fibrous rubbery polymer. The

polymer was scraped out, cut up, and blended with methanol in a blender and then stirred with fresh boiling methanol for 1 hr. The white rubber was dried under high vacuum for 3 days to yield 9.6 g (7270 catalyst turnovers) of rubbery polyethylene.  $^1\text{H}$  NMR analysis ( $\text{CDCl}_3$ ): 95 methyl carbons per 1000 methylene carbons.

Differential scanning calorimetry:  $-51^\circ\text{C}$  ( $T_g$ ); mp:  $39.5^\circ\text{C}$  (4J/g); mp:  $76.4^\circ\text{C}$  (7J/g). Gel permeation chromatography (trichlorobenzene,  $135^\circ\text{C}$ , polystyrene reference, results calculated as polyethylene using universal calibration theory):  $M_n=223,000$ ;  $M_w=487,000$ ;  $M_w/M_n=2.19$ .

The polyethylene of Example 83 could be cast from hot chlorobenzene or pressed at  $200^\circ\text{C}$  to give a strong, stretchy, hazy, transparent film with good recovery. It was not easily chloroform-soluble. This example demonstrates the use of the catalyst's ability (see Example 82) to make both amorphous and crystalline polymer, and to make both types of polymer within the same polymer chain due to the catalyst's low propensity to chain transfer. With crystalline blocks (due to higher ethylene pressure) on both ends and an amorphous region (due to lower- pressure, mass transfer-limited polymerization) in the center of each chain, this polymer is a thermoplastic elastomer.

#### Example 84

A Schlenk flask containing 147 mg (0.100 mmol) of  $\{[(2,6\text{-i-PrPh})\text{DABMe}_2]\text{PdMe}(\text{OEt}_2)\}\text{BAF}^-$  was cooled to  $-78^\circ\text{C}$ , evacuated, and placed under an ethylene atmosphere. Methylene chloride (100 ml) was added to the flask and the solution was then allowed to warm to room temperature and stirred. The reaction vessel was warm during the first several hours of mixing and the solution became viscous. After being stirred for 17.4 h, the reaction mixture was added to  $\sim 600$  mL of MeOH in order to precipitate the polymer. Next, the MeOH was decanted off of the sticky polymer, which was then

dissolved in ~600 mL of petroleum ether. After being filtered through plugs of neutral alumina and silica gel, the solution appeared clear and almost colorless. The solvent was then removed and the viscous oil (45.31 g) was dried in vacuo for several days:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  1.24 ( $\text{CH}_2$ , CH), 0.82 (m,  $\text{CH}_3$ ); Branching: ~128  $\text{CH}_3$  per 1000  $\text{CH}_2$ ; DSC:  $T_g = -67.7^\circ\text{C}$ . GPC:  $M_n = 29,000$ ;  $M_w = 112,000$ .

#### Example 85

Following the procedure of Example 84  $\{[(2,6\text{-i-PrPh})\text{DABMe}_2]\text{PdMe}(\text{OEt}_2)\}\text{BAF}^-$  (164 mg, 0.112 mmol) catalyzed the polymerization of ethylene for 24 h in 50 mL of  $\text{CH}_2\text{Cl}_2$  to give 30.16 g of polymer as a viscous oil.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  1.41 ( $\text{CH}_2$ , CH), 0.94 ( $\text{CH}_3$ ); Branching: ~115  $\text{CH}_3$  per 1000  $\text{CH}_2$ ; GPC Analysis (THF, PMMA standards, RI Detector):  $M_w = 262,000$ ;  $M_n = 121,000$ ; PDI = 2.2; DSC:  $T_g = -66.8^\circ\text{C}$ .

#### Example 86

The procedure of Example 84 was followed using 144 mg (0.100 mmol) of  $\{[(2,6\text{-i-PrPh})\text{DABH}_2]\text{PdMe}(\text{OEt}_2)\}\text{BAF}^-$  in 50 mL of  $\text{CH}_2\text{Cl}_2$  and a 24 h reaction time. Polymer (9.68 g) was obtained as a free-flowing oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  5.36 (m,  $\text{RHC=CHR}'$ ), 5.08 (br s,  $\text{RR}'\text{C=CHR}'$ ), 4.67 (br s,  $\text{H}_2\text{C=CRR}'$ ), 1.98 (m, allylic H), 1.26 ( $\text{CH}_2$ , CH), 0.83 (m,  $\text{CH}_3$ ); Branching: ~149  $\text{CH}_3$  per 1000  $\text{CH}_2$ ; DSC:  $T_g = -84.6^\circ\text{C}$ .

#### Example 87

A 30-mg (0.042-mmol) sample of  $[(2,6\text{-i-PrPh})\text{DABAn}]\text{NiBr}_2$  was placed in Parr® 600-mL stirred autoclave under nitrogen. The autoclave was sealed and 150 mL of dry toluene and 0.6 mL of 3M polymethylalumoxane were injected into the autoclave through the head port. The autoclave body was immersed in a flowing water bath and the mixture was stirred under nitrogen at  $20^\circ\text{C}$  for 1 hr. The autoclave was then pressurized with ethylene to 1.31 MPa with stirring for 5 min as the internal temperature peaked at  $30^\circ\text{C}$ . The ethylene was then vented to 41.4 kPa

(gauge) and the mixture was stirred and fed ethylene at 41.4 kPa for 1.5 hr as the internal temperature dropped to 19°C. At the end of this time, the autoclave was again pressurized to 1.34 MPa and stirred for 7 min as the internal temperature rose to 35°C.

The ethylene was vented and the autoclave was briefly evacuated; the product was a stiff, solvent-swollen gel. The polymer was cut up, blended with 500 mL methanol in a blender, and then stirred overnight with 500 mL methanol containing 10 mL of 6N HCl. The stirred suspension in methanol/HCl was then boiled for 4 hr, filtered, and dried under high vacuum overnight to yield 26.1 g (22,300 catalyst turnovers) of polyethylene. Differential scanning calorimetry: -49°C (T<sub>g</sub>); mp: 116°C (42J/g). The melting transition was very broad and appeared to begin around room temperature. Although the melting point temperature is higher in this Example than in Example 76, the area under the melting endotherm is less in this example, implying that the polymer of this Example is less crystalline overall, but the crystallites that do exist are more ordered. This indicates that the desired block structure was obtained. Gel permeation chromatography (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal calibration theory): M<sub>n</sub>=123,000; M<sub>w</sub>=601,000; M<sub>w</sub>/M<sub>n</sub>=4.87. The polyethylene of this example could be pressed at 200°C to give a strong, tough, stretchy, hazy film with partial elastic recovery. When the stretched film was plunged into boiling water, it completely relaxed to its original dimensions.

#### Example 88

A 6.7-mg (0.011-mmol) sample of [(2,6-i-PrPh)DABMe<sub>2</sub>]NiBr<sub>2</sub> was magnetically-stirred under nitrogen in a 50-mL Schlenk flask with 25 mL of dry, deaerated toluene as 0.3 mL of 3M poly(methylalumoxane) was injected via syringe. The mixture was stirred at 23°C for 40 min to give a deep blue-green solution of



catalyst. Dry, deaerated cyclopentene (10 mL) was injected and the mixture was stirred for 5 min. The flask was then pressurized with ethylene at 20.7 MPa and stirred for 22 hr. The resulting viscous solution was poured into a stirred mixture of 200 mL methanol and 10 mL 6N HCl. The methanol was decanted off and replaced with fresh methanol, and the polymer was stirred in boiling methanol for 3 hr. The tough, stretchy rubber was pressed between paper towels and dried under vacuum to yield 1.0g of poly[ethylene/cyclopentene]. By  $^1\text{H}$  NMR analysis( $\text{CDCl}_3$ ): 100 methyl carbons per 1000 methylene carbons. Comparison of the peaks attributable to cyclopentene (0.65 ppm and 1.75 ppm) with the standard polyethylene peaks (0.9 ppm and 1.3 ppm) indicates about a 10 mol% cyclopentene incorporation. This polymer yield and composition represent about 2900 catalyst turnovers. Differential scanning calorimetry: -44°C (Tg). Gel permeation chromatography (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal calibration theory):  $M_n=122,000$ ;  $M_w=241,000$ ;  $M_w/M_n=1.97$ .

Listed below are the  $^{13}\text{C}$  NMR data upon which the above analysis is based.

$^{13}\text{C}$ NMR data		
TCB, 120C, 0.05M CrAcAc		
Freq ppm	Intensity	
50.9168	5.96663	
46.3865	3.27366	1 cme and/or 1,3 ccmcc
40.7527	40.5963	2 eme
40.567	41.9953	1,3 eme
40.3336	45.8477	1,3 eme
37.1985	60.1003	
36.6998	41.2041	
36.0579	11.2879	
35.607	25.169	
34.4771	19.0834	
34.0845	22.8886	
33.1243	20.1138	
32.8962	27.6778	
31.8406	75.2391	
30.0263	76.2755	

29.6921	170.41	
28.9494	18.8754	
28.647	25.8032	
27.4588	22.2397	
27.1086	48.0806	
24.3236	3.31441	
22.5783	4.64411	2B <sub>5</sub> +, 2 EOC
19.6712	43.1867	1B <sub>1</sub>
17.5546	1.41279	end group
14.3399	1.74854	1B <sub>3</sub>
13.8518	5.88699	1B <sub>4</sub> +, 1EOC
10.9182	2.17785	2B <sub>1</sub>

Example 89

A 7.5-mg (0.013-mmol) sample of [(2,6-t-BuPh)<sub>2</sub>DABMe<sub>2</sub>]<sub>2</sub>NiBr<sub>2</sub> was magnetically stirred under  
 5 nitrogen in a 50-mL Schlenk flask with 40 mL of dry, deaerated toluene as 0.5 mL of 3M poly(methylalumoxane) was injected via syringe. The mixture was stirred at 23°C for 1 hr to give a deep blue-green solution of catalyst. The flask was pressurized with ethylene at  
 10 20.7 kPa (gauge) and stirred for 20 hr. The solution, which had become a reddish-brown suspension, was poured into a stirred mixture of 200 mL methanol and 10 mL 6N HCl and was stirred at reflux for 1 hr. The methanol was decanted off and replaced with fresh methanol, and  
 15 the white polymer was stirred in boiling methanol for 1 hr. The stiff, stretchy rubber was pressed between paper towels and then dried under vacuum to yield 1.25 g (3380 catalyst turnovers) of polyethylene. <sup>1</sup>H-1 NMR analysis (C<sub>6</sub>D<sub>6</sub>): 63 methyl carbons per 1000 methylene  
 20 carbons. Differential scanning calorimetry: -34°C (T<sub>g</sub>); mp: 44°C (31J/g); mp: 101°C (23J/g).

Example 90

A 5.5 mg (0.0066 mmol) sample of {[(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>]<sub>2</sub>PdMe(Et<sub>2</sub>O)}<sup>+</sup>SbF<sub>6</sub><sup>-</sup> was allowed to stand at  
 25 room temperature in air for 24 hr. A 100-mL three-neck flask with a magnetic stirrer and a gas inlet dip tube was charged with 40 mL of reagent methylene chloride and ethylene gas was bubbled through with stirring to saturate the solvent with ethylene. The sample of  
 30 {[(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>]<sub>2</sub>PdMe(Et<sub>2</sub>O)}<sup>+</sup>SbF<sub>6</sub><sup>-</sup> was then rinsed

into the flask with 5 mL of methylene chloride and ethylene was bubbled through with stirring for 5 hr. The clear yellow solution was rotary evaporated to yield 0.20 g (1080 catalyst turnovers) of a thick yellow liquid polyethylene.

#### Example 91

A 600-mL stirred Parr® autoclave was sealed and flushed with nitrogen, and 100 mL of dry, deaerated toluene was introduced into the autoclave via gas tight syringe through a port on the autoclave head. The autoclave was purged with propylene gas to saturate the solvent with propylene. Then 45 mg (0.054 mmol) of  $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdMe}(\text{Et}_2\text{O})\}\text{SbF}_6^-$  was introduced into the autoclave in the following manner: a 2.5-mL gas tight syringe with a syringe valve was loaded with 45 mg of  $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdMe}(\text{Et}_2\text{O})\}\text{SbF}_6^-$  under nitrogen in a glove box; then 1-2 mL of dry, deaerated methylene chloride was drawn up into the syringe and the contents were quickly injected into the autoclave through a head port. This method avoids having the catalyst in solution with no stabilizing ligands.

The autoclave was pressurized with propylene to 41.4 MPa and stirred for 2.5 hr, starting with continuous propylene feed. The autoclave was cooled in a running tap water bath at 22°C. The internal temperature quickly rose to 30°C upon initial propylene addition but soon dropped back to 22°C. After 0.5 hr, the propylene feed was shut off and stirring was continued. Over 2 hr, the pressure dropped from 41.4 MPa to 38.6 MPa. The propylene was then vented. The product was a thin, honey-colored solution. Rotary evaporation yielded 2.3 g (1010 catalyst turnovers) of very thick, dark-brown liquid polypropylene which was almost elastomeric when cool. Gel permeation chromatography (trichlorobenzene, 135°C, polystyrene reference, results calculated as polypropylene using universal calibration theory):  $M_n=8,300$ ;  $M_w=15,300$ ;  $M_w/M_n=1.84$ .  $^{13}\text{C}$  NMR analysis; branching per 1000  $\text{CH}_2$ :

total Methyls (545), Propyl (1.3),  $\geq$ Butyl and end of chain (9.2); chemical shifts. The polymer exhibited a glass transition temperature of  $-44^{\circ}\text{C}$  by differential scanning calorimetry.

- 5 Listed below are the  $^{13}\text{C}$  NMR data upon which the above analysis is based.

$^{13}\text{C}$  NMR data

CDCl <sub>3</sub> , RT, 0.05M CrAcAc		
Freq ppm	Intensity	
46.4978	13.2699	Methylenes
45.8683	11.9947	Methylenes
45.3639	10.959	Methylenes
45.1783	11.3339	Methylenes
44.5568	8.41708	Methylenes
44.4398	7.69019	Methylenes
44.3026	6.29108	Methylenes
44.1372	6.73541	Methylenes
43.5036	5.49837	Methylenes
42.4262	5.03113	Methylenes
41.6918	3.72552	Methylenes
39.1537	4.23147	Methines and Methylenes
38.7179	25.2596	Methines and Methylenes
37.8664	10.0979	Methines and Methylenes
37.6727	14.3755	Methines and Methylenes
37.0755	17.623	Methines and Methylenes
36.781	42.0719	Methines and Methylenes
36.559	10.0773	Methines and Methylenes
34.5495	5.34388	Methines and Methylenes
34.3195	7.48969	Methines and Methylenes
33.5488	12.6148	Methines and Methylenes
33.351	20.5271	Methines and Methylenes
32.7982	4.10612	Methines and Methylenes
32.4108	22.781	Methines and Methylenes
31.8701	5.90488	Methines and Methylenes
31.5957	10.6988	Methines and Methylenes
29.8364	44.4935	Methines and Methylenes
29.7072	103.844	Methines and Methylenes
29.3925	152.645	Methines and Methylenes
29.0293	6.71341	Methines and Methylenes
27.6089	38.7993	Methines and Methylenes
27.4193	10.3543	Methines and Methylenes
27.0763	66.8261	Methines and Methylenes
26.9552	92.859	Methines and Methylenes
26.7615	55.7233	Methines and Methylenes
26.3661	20.1674	Methines and Methylenes
24.8529	16.9056	Methine Carbon of XXVIII
23.1217	12.5439	Methine carbons of XXVIII and XXIX, 2B <sub>4</sub> <sup>+</sup> , EOC
22.6779	13.0147	Methine carbons of XXVIII and XXIX, 2B <sub>4</sub> <sup>+</sup> , EOC
22.5245	9.16236	Methine carbons of XXVIII and XXIX, 2B <sub>4</sub> <sup>+</sup> , EOC

22.3389	77.3342	Methine carbons of XXVIII and XXIX, 2B <sub>4</sub> <sup>+</sup> , EOC
21.9757	9.85242	Methine carbons of XXVIII and XXIX, 2B <sub>4</sub> <sup>+</sup> , EOC
21.1405	10.0445	Methyls
20.4182	8.49663	Methyls
19.9743	25.8085	Methyls
19.825	31.4787	Methyls
19.3811	44.9986	Methyls
19.1995	31.3058	Methyls
13.8569	6.37761	Methyls
13.8004	7.67242	Methyls
137.452	22.0529	Methyls
128.675	44.6993	Methyls
127.88	43.8939	Methyls
124.959	22.4025	Methyls
122.989	3.3312	Methyls

Example 92

A 600-mL stirred Parr® autoclave was sealed, flushed with nitrogen, and heated to 60°C in a water bath. Fifty mL (48 g; 0.56 mol) of dry, deaerated methyl acrylate was introduced into the autoclave via gas tight syringe through a port on the autoclave head and ethylene gas was passed through the autoclave at a low rate to saturate the solvent with ethylene before catalyst addition. Then 60 mg (0.07 mmol) of {[(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>]PdMe(Et<sub>2</sub>O)}SbF<sub>6</sub><sup>-</sup> was introduced into the autoclave in the following manner: a 2.5-mL gas tight syringe with a syringe valve was loaded with 60 mg of {[(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>]PdMe(Et<sub>2</sub>O)}SbF<sub>6</sub><sup>-</sup> under nitrogen in a glove box; then 1 mL of dry, deaerated methylene chloride was drawn up into the syringe and the contents were quickly injected into the autoclave through a head port. This method avoids having the catalyst in solution with no stabilizing ligands.

The autoclave was pressurized with ethylene to 689 kPa and continuously fed ethylene with stirring for 4.5 hr; the internal temperature was very steady at 60°C. The ethylene was vented and the product, a clear yellow solution, was rinsed out of the autoclave with chloroform, rotary evaporated, and held under high vacuum overnight to yield 1.56 g of thin light-brown liquid ethylene/methyl acrylate copolymer. The

infrared spectrum of the product exhibited a strong ester carbonyl stretch at  $1740\text{ cm}^{-1}$ .  $^1\text{H}$ -1 NMR analysis ( $\text{CDCl}_3$ ): 61 methyl carbons per 1000 methylene carbons. Comparison of the integrals of the ester methoxy (3.67ppm) and ester methylene ( $\text{CH}_2\text{COOMe}$ ; 2.30ppm) peaks with the integrals of the carbon chain methyls (0.8-0.9ppm) and methylenes (1.2-1.3ppm) indicated a methyl acrylate content of 16.6 mol% (37.9 wt%). This product yield and composition represent 480 ethylene turnovers and 96 methyl acrylate turnovers.  $^{13}\text{C}$  NMR analysis; branching per 1000  $\text{CH}_2$ : total methyls (48.3), Methyl (20.8), Ethyl (10.5), Propyl (1), Butyl (8),  $\geq$ Amyl and End of Chain (18.1), methyl acrylate (94.4); ester-bearing  $-\text{CH}(\text{CH}_2)_n\text{CO}_2\text{CH}_3$  branches as a % of total ester:  $n \geq 5$  (35.9),  $n=4$  (14.3),  $n=1,2,3$  (29.5),  $n=0$  (20.3); chemical shifts were referenced to the solvent: the high field carbon of 1,2,4-trichlorobenzene (127.8 ppm). Gel permeation chromatography (tetrahydrofuran,  $30^\circ\text{C}$ , polymethylmethacrylate reference, results calculated as polymethylmethacrylate using universal calibration theory):  $M_n=3,370$ ;  $M_w=5,450$ ;  $M_w/M_n=1.62$ .

Listed below are the  $^{13}\text{C}$  NMR data upon which the above analysis is based.

<sup>13</sup>C NMR data

TCB 120C, 0.05M CrAcAc		
Freq ppm	Intensity	
53.7443	2.19635	CH <sub>2</sub> Cl <sub>2</sub> solvent impurity
50.9115	8.84408	
50.641	132.93	
45.5165	7.55996	MEB <sub>0</sub> 43.8 ppm:2 adjacent MEB <sub>0</sub>
39.6917	2.71676	
39.2886	7.91933	
38.1639	13.843	
37.7926	26.6353	
37.1666	20.6759	
36.6733	8.65855	
34.6256	17.6899	
34.4612	16.7388	
34.1429	85.624	
33.9095	124.997	1EB <sub>4</sub> +
33.676	40.0271	Contributions from EB
33.2888	11.4719	Contributions from EB
32.8644	14.4963	Contributions from EB
32.3498	17.5883	Contributions from EB
32.0475	9.83096	Contributions from EB
31.8459	30.9676	Contributions from EB
31.7079	12.7737	Contributions from EB
31.5912	13.8792	Contributions from EB
31.0873	19.6266	Contributions from EB
30.6258	10.5512	
30.1324	58.6101	
29.6497	169.398	
29.4322	48.5318	
29.1934	95.4948	
27.8619	8.70181	
27.4269	32.9529	
26.9283	78.0563	
26.5145	27.0608	
26.3554	14.0683	
25.4588	21.9081	2EB <sub>4</sub> (tent)
25.3315	9.04646	2EB <sub>4</sub> (tent)
24.9761	64.2333	2EB <sub>5</sub> +
24.2069	10.771	BBB (beta-beta-B)
23.0451	9.50073	2B <sub>4</sub>
22.9337	6.90528	2B <sub>4</sub>
22.5518	30.0427	2B <sub>5</sub> +, EOC
19.9842	1.87415	2B <sub>3</sub>
19.6288	17.125	1B <sub>1</sub>
19.1673	6.0427	1B <sub>1</sub>
16.7695	2.23642	
14.3	-	1B <sub>3</sub>
13.7882	34.0749	1B <sub>4</sub> +, EOC
11.0774	4.50599	1B <sub>2</sub>
10.8705	10.8817	1B <sub>2</sub>
189.989	1.04646	EB <sub>0</sub> Carbonyl
175.687	3.33867	EB <sub>0</sub> Carbonyl
175.406	14.4124	EB <sub>0</sub> Carbonyl
175.22	5.43832	EB <sub>0</sub> Carbonyl
175.061	3.53125	EB <sub>0</sub> Carbonyl

172.859	11.2356	EB <sub>1</sub> + Carbonyl
172.605	102.342	EB <sub>1</sub> + Carbonyl
172.09	7.83303	EB <sub>1</sub> + Carbonyl
170.944	3.294	EB <sub>1</sub> + Carbonyl

Example 93

A 45-mg (0.048-mmol) sample of  $\{[(2,6-i-PrPh)_2DABAn]PdMe(Et_2O)\}SbF_6^-$  was placed in a 600-mL Parr  
 5 ® stirred autoclave under nitrogen. To this was added 50 mL of dry, deaerated methylene chloride, and the autoclave was pressurized to 414 kPa with ethylene. Ethylene was continuously fed at 414 kPa with stirring at 23-25°C for 3 hr; then the feed was shut off and the  
 10 reaction was stirred for 12 hr more. At the end of this time, the autoclave was under 89.6 kPa (absolute). The autoclave was repressurized to 345 kPa with ethylene and stirred for 2 hr more as the pressure dropped to 255 kPa, showing that the catalyst was still  
 15 active; the ethylene was then vented. The brown solution in the autoclave was rotary evaporated, taken up in chloroform, filtered through alumina to remove catalyst, and rotary evaporated and then held under high vacuum to yield 7.35 g of thick, yellow liquid  
 20 polyethylene. <sup>1</sup>H NMR analysis (CDCl<sub>3</sub>): 131 methyl carbons per 1000 methylene carbons. Gel permeation chromatography (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal calibration theory): M<sub>n</sub>=10,300; M<sub>w</sub>=18,100;  
 25 M<sub>w</sub>/M<sub>n</sub>=1.76.

Example 94

A 79-mg (0.085-mmol) sample of  $\{[(2,6-i-PrPh)_2DABAn]PdMe(Et_2O)\}SbF_6^-$  was placed in a 600-mL Parr  
 30 ® stirred autoclave under nitrogen. To this was added 50 mL of dry, deaerated methyl acrylate, and the autoclave was pressurized to 689 kPa with ethylene. The autoclave was warmed to 50°C and the reaction was stirred at 689 kPa for 70 hr; the ethylene was then vented. The clear yellow solution in the autoclave was  
 35 filtered through alumina to remove catalyst, rotary



evaporated, and held under high vacuum to yield 0.27 g of liquid ethylene/methyl acrylate copolymer. The infrared spectrum of the product exhibited a strong ester carbonyl stretch at  $1740\text{cm}^{-1}$ .  $^1\text{H}$  NMR analysis (CDCl<sub>3</sub>): 70 methyl carbons per 1000 methylene carbons; 13.5 mol% (32 wt%) methyl acrylate. This yield and composition represent 12 methyl acrylate turnovers and 75 ethylene turnovers.

#### Example 95

10 A 67-mg (0.089-mmol) of  $\{[(2,4,6\text{-MePh})_2\text{DABMe}_2]\text{PdMe}(\text{Et}_2\text{O})\}\text{SbF}_6^-$  was placed in a 200-mL glass centrifuge bottle with a magnetic stir bar under nitrogen. To this was added 40 mL of dry, deaerated methylene chloride. The bottle was immediately  
15 pressurized to 207 kPa with ethylene. Ethylene was continuously fed at 207 kPa with stirring at 23-25°C for 4 hr. After 4 hr, the ethylene feed was shut off and the reaction was stirred for 12 hr more. At the end of this time, the bottle was under zero pressure  
20 (gauge). The brown solution was rotary evaporated and held under high vacuum to yield 5.15 g of thick, brown liquid polyethylene.  $^1\text{H}$  NMR analysis (CDCl<sub>3</sub>): 127 methyl carbons per 1000 methylene carbons. Gel permeation chromatography (trichlorobenzene, 135°C, polystyrene reference, results calculated as  
25 polyethylene using universal calibration theory):  $M_n=20,200$ ;  $M_w=32,100$ ;  $M_w/M_n=1.59$ .

#### Example 96

A 56-mg (0.066-mmol) sample of  $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdCH}_2\text{CH}_2\text{C}(\text{O})\text{CH}_3\}\text{SbF}_6^-$  was placed in a 600-mL Parr® stirred autoclave under nitrogen. To this was added 30 mL of dry, deaerated perfluoro(propyltetrahydrofuran). The autoclave was stirred and pressurized to 5.9 MPa with ethylene. The  
35 internal temperature peaked at 29°C; a cool water bath was placed around the autoclave body. The reaction was stirred for 16 hr at 23°C and 5.9 MPa and the ethylene was then vented. The autoclave contained a light

yellow granular rubber; this was scraped out of the autoclave and held under high vacuum to yield 29.0 g (15,700 catalyst turnovers) of spongy, non-tacky, rubbery polyethylene which had good elastic recovery and was very strong; it was soluble in chloroform or chlorobenzene.

The polyethylene was amorphous at room temperature: it exhibited a glass transition temperature of  $-57^{\circ}\text{C}$  and a melting endotherm of  $-16^{\circ}\text{C}$  (35J/g) by differential scanning calorimetry. On cooling, there was a crystallization exotherm with a maximum at  $1^{\circ}\text{C}$  (35J/g). Upon remelting and recooling the melting endotherm and crystallization exotherm persisted, as did the glass transition. Dynamic mechanical analysis at 1Hz showed a  $\tan \delta$  peak at  $-51^{\circ}\text{C}$  and a peak in the loss modulus  $E''$  at  $-65^{\circ}\text{C}$ ; dielectric analysis at 1000 Hz showed a  $\tan d$  peak at  $-35^{\circ}\text{C}$ .  $^1\text{H}$  NMR analysis ( $\text{CDCl}_3$ ): 86 methyl carbons per 1000 methylene carbons.  $^{13}\text{C}$  NMR analysis: branching per 1000  $\text{CH}_2$ : total Methyls (89.3), Methyl (37.2), Ethyl (14), Propyl (6.4), Butyl (6.9),  $\geq\text{Am}$  and End Of Chain (23.8); chemical shifts were referenced to the solvent: the high field carbon of 1,2,4-trichlorobenzene (127.8 ppm). Gel permeation chromatography (trichlorobenzene,  $135^{\circ}\text{C}$ , polystyrene reference, results calculated as polyethylene using universal calibration theory):  $M_n=137,000$ ;  $M_w=289,000$ ;  $M_w/M_n=2.10$ . Intrinsic viscosity (trichlorobenzene,  $135^{\circ}\text{C}$ ): 2.565 dL/g. Absolute molecular weight averages corrected for branching:  $M_n=196,000$ ;  $M_w=425,000$ ;  $M_w/M_n=2.17$ . Density (determined at room temperature with a helium gas displacement pycnometer):  $0.8546 \pm 0.0007$  g/cc.

#### Example 97

A 49-mg (0.058 mmol) sample of  $\{[(2,6\text{-i-PrPh})_2\text{DABMe}] \text{PdCH}_2\text{CH}_2\text{C}(\text{O})\text{CH}_3\} \text{SbF}_6^-$  was placed in a 600-mL Parr® stirred autoclave under nitrogen. To this was added 30 mL of dry, deaerated hexane. The autoclave was stirred and pressurized to 5.9 MPa with ethylene.

The internal temperature peaked briefly at 34°C; a cool water bath was placed around the autoclave body. The reaction was stirred for 16 hr at 23°C. At 14 hr, the ethylene feed was shut off; the autoclave pressure  
5 dropped to 5.8 MPa over 2 hr; the ethylene was then vented. The autoclave contained a light yellow, gooey rubber swollen with hexane, which was scraped out of the autoclave and held under high vacuum to yield 28.2 g (17,200 catalyst turnovers) of spongy, non-tacky,  
10 rubbery polyethylene which had good elastic recovery and which was very strong.

The polyethylene was amorphous at room temperature: it exhibited a glass transition temperature of -61°C and a melting endotherm of -12°C  
15 (27J/g) by differential scanning calorimetry. Dynamic mechanical analysis at 1Hz showed a tan  $\delta$  peak at -52°C and a peak in the loss modulus  $E''$  at -70°C; dielectric analysis at 1000 Hz showed a tan  $\delta$  peak at -37°C.  $^1\text{H}$  NMR analysis ( $\text{CDCl}_3$ ): 93 methyl carbons per 1000  
20 methylene carbons.  $^{13}\text{C}$  NMR analysis: branching per 1000  $\text{CH}_2$ : total Methyls (95.4), Methyl (33.3), Ethyl (17.2), Propyl (5.2), Butyl (10.8), Amyl (3.7),  $\geq\text{Hex}$  and End Of Chain (27.4); chemical shifts were referenced to the solvent: the high field carbon of  
25 1,2,4-trichlorobenzene (127.8 ppm). Gel permeation chromatography (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal calibration theory):  $M_n=149,000$ ;  $M_w=347,000$ ;  $M_w/M_n=2.33$ . Density (determined at room temperature  
30 with a helium gas displacement pycnometer):  $0.8544 \pm 0.0007$  g/cc.

#### Example 98

Approximately 10-mesh silica granules were dried at 200°C and were impregnated with a methylene chloride  
35 solution of  $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdCH}_2\text{CH}_2\text{C(O)CH}_3\}\text{SbF}_6^-$  to give a 10 wt% loading of the catalyst on silica.

A 0.53-g (0.063 mmol) sample of silica gel containing 10 wt%  $\{[(2,6\text{-i-}$

$(\text{PrPh})_2\text{DABMe}_2\text{PdCH}_2\text{CH}_2\text{C}(\text{O})\text{CH}_3\text{SbF}_6^-$  was placed in a 600-mL Parr® stirred autoclave under nitrogen. To this was added 40 mL of dry, deaerated hexane. The autoclave was stirred and pressurized to 5.5 MPa with ethylene; the ethylene feed was then turned off. The internal temperature peaked briefly at 31°C. The reaction was stirred for 14 hr at 23°C as the pressure dropped to 5.3 MPa; the ethylene was then vented. The autoclave contained a clear, yellow, gooey rubber swollen with hexane. The product was dissolved in 200 mL chloroform, filtered through glass wool, rotary evaporated, and held under high vacuum to yield 7.95 g (4500 catalyst turnovers) of gummy, rubbery polyethylene.  $^1\text{H}$  NMR analysis ( $\text{CDCl}_3$ ): 96 methyl carbons per 1000 methylene carbons. Gel permeation chromatography (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal calibration theory):  $M_n=6,900$ ;  $M_w=118,000$ ;  $M_w/M_n=17.08$ .

20 Example 99

A 108-mg (0.073 mmol) sample of  $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2\text{PdCH}_2\text{CH}_2\text{C}(\text{O})\text{CH}_3]\text{BAF}^-\}$  was placed in a 600-mL Parr® stirred autoclave under nitrogen. To this was added via syringe 75 mL of deaerated reagent grade methyl acrylate containing 100 ppm hydroquinone monomethyl ether and 100 ppm of phenothiazine. The autoclave was pressurized to 5.5 MPa with ethylene and was stirred at 35°C as ethylene was continuously fed for 90 hr; the ethylene was then vented. The product consisted of a swollen clear foam wrapped around the impeller; 40 mL of unreacted methyl acrylate was poured off the polymer. The polymer was stripped off the impeller and was held under high vacuum to yield 38.2 g of clear, grayish, somewhat-tacky rubber.  $^1\text{H}$  NMR analysis ( $\text{CDCl}_3$ ): 99 methyl carbons per 1000 methylene carbons. Comparison of the integrals of the ester methoxy (3.67ppm) and ester methylene ( $\text{CH}_2\text{COOMe}$ ; 2.30ppm) peaks with the integrals of the carbon chain

methyls (0.8-0.9ppm) and methylenes (1.2-1.3ppm) indicated a methyl acrylate content of 0.9 mol% (2.6 wt%). This product yield and composition represent 18,400 ethylene turnovers and 158 methyl acrylate  
5 turnovers.  $^{13}\text{C}$  NMR analysis: branching per 1000  $\text{CH}_2$ : total Methyls (105.7), Methyl (36.3), Ethyl (22), Propyl (4.9), Butyl (10.6), Amyl (4),  $\geq\text{Hex}$  and End Of Chain (27.8), methyl acrylate (3.4); ester-bearing  $-\text{CH}(\text{CH}_2)_n\text{CO}_2\text{CH}_3$  branches as a % of total ester:  $n \geq 5$   
10 (40.6),  $n=1,2,3$  (2.7),  $n=0$  (56.7); chemical shifts were referenced to the solvent: the high field carbon of 1,2,4-trichlorobenzene (127.8 ppm). Gel permeation chromatography (tetrahydrofuran,  $30^\circ\text{C}$ , polymethylmethacrylate reference, results calculated as  
15 polymethylmethacrylate using universal calibration theory):  $M_n=151,000$ ;  $M_w=272,000$ ;  $M_w/M_n=1.81$ .

#### Example 100

A 62-mg (0.074-mmol) sample of  $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdMe}(\text{Et}_2\text{O})\}\text{SbF}_6^-$  was placed in a  
20 600-mL Parr® stirred autoclave under nitrogen with 200 mL of deaerated aqueous 10% (v/v) n-butanol. The autoclave was pressurized to 2.8 MPa with ethylene and was stirred for 16 hr. The ethylene was vented and the polymer suspension was filtered. The product consisted  
25 of a fine gray powdery polymer along with some larger particles of sticky black polymer; the polymer was washed with acetone and dried to yield 0.60 g (290 catalyst turnovers) of polyethylene. The gray polyethylene powder was insoluble in chloroform at RT;  
30 it was soluble in hot tetrachloroethane, but formed a gel on cooling to RT.  $^1\text{H}$  NMR analysis (tetrachloroethane- $d_2$ ;  $100^\circ\text{C}$ ): 43 methyl carbons per 1000 methylene carbons. Differential scanning calorimetry exhibited a melting point at  $89^\circ\text{C}$  (78J/g)  
35 with a shoulder at  $70^\circ\text{C}$ ; there was no apparent glass transition.

#### Example 101

A 78-mg (0.053-mmol) sample of  $\{[(2,6-i-PrPh)_2DABMe_2]PdCH_2CH_2C(O)CH_3\}BAF^-$  was placed in a 600-mL Parr® stirred autoclave under nitrogen. To this was added 40 mL of dry, deaerated t-butyl acrylate containing 100 ppm hydroquinone monomethyl ether. The autoclave was pressurized with ethylene to 2.8 MPa and was stirred and heated at 35°C as ethylene was continuously fed at 2.8 MPa for 24 hr; the ethylene was then vented. The product consisted of a yellow, gooey polymer which was dried under high vacuum to yield 6.1 g of clear, yellow, rubbery ethylene/t-butyl acrylate copolymer which was quite tacky.  $^1H$  NMR analysis ( $CDCl_3$ ): 102 methyl carbons per 1000 methylene carbons. Comparison of the integral of the ester t-butoxy (1.44 ppm) peak with the integrals of the carbon chain methyls (0.8-0.9ppm) and methylenes (1.2-1.3ppm) indicated a t-butyl acrylate content of 0.7 mol% (3.3 wt%). This yield and composition represent 3960 ethylene turnovers and 30 t-butyl acrylate turnovers. Gel permeation chromatography (tetrahydrofuran, 30°C, polymethylmethacrylate reference, results calculated as polymethylmethacrylate using universal calibration theory):  $M_n=112,000$ ;  $M_w=179,000$ ;  $M_w/M_n=1.60$ .

#### Example 102

A 19-mg (0.022-mmol) sample of  $\{[(2,6-i-PrPh)_2DABMe_2]PdCH_2CH_2C(O)CH_3\}SbF_6^-$  was placed in a 600-mL Parr® stirred autoclave under nitrogen. The autoclave was pressurized to 5.2 MPa with ethylene and was stirred for 2 hr; the ethylene feed was then shut off. The autoclave was stirred for 16 hr more as the ethylene pressure dropped to 5.0 MPa; the ethylene was then vented. The autoclave contained a light yellow, granular sponge rubber growing all over the walls and head of the autoclave; this was scraped out to yield 13.4 g (21,800 catalyst turnovers) of spongy, non-tacky, rubbery polyethylene which was very strong and elastic.  $^1H$  NMR analysis ( $CDCl_3$ ): 90 methyl carbons per 1000 methylene carbons.

Differential scanning calorimetry exhibited a glass transition at  $-50^{\circ}\text{C}$ . Gel permeation chromatography (trichlorobenzene,  $135^{\circ}\text{C}$ , polystyrene reference, results calculated as polyethylene using universal calibration theory):  $M_n=175,000$ ;  $M_w=476,000$ ;  $M_w/M_n=2.72$ .

#### Example 103

A 70-mg (0.047-mmol) sample of  $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdCH}_2\text{CH}_2\text{C}(\text{O})\text{CH}_3\}\text{BAF}^+$  was placed in a 600-mL Parr® stirred autoclave under nitrogen. To this was added 70 mL of deaerated reagent grade methyl acrylate containing 100 ppm each hydroquinone monomethyl ether and phenothiazine and 0.7 mL (1 wt%; 4.7 mol%) deaerated, deionized water. The autoclave was stirred at  $35^{\circ}\text{C}$  as ethylene was continuously fed at 4.8 MPa for 16 hr; the ethylene was then vented. The product consisted of a clear solution. Rotary evaporation yielded 1.46 g of ethylene/methyl acrylate copolymer as a clear oil. The infrared spectrum of the product exhibited a strong ester carbonyl stretch at  $1740\text{cm}^{-1}$ .  $^1\text{H}$  NMR analysis ( $\text{CDCl}_3$ ): 118 methyl carbons per 1000 methylene carbons. Comparison of the integrals of the ester methoxy (3.67ppm) and ester methylene ( $\text{CH}_2\text{COOMe}$ ; 2.30ppm) peaks with the integrals of the carbon chain methyls (0.8-0.9ppm) and methylenes (1.2-1.3ppm) indicated a methyl acrylate content of 0.7 mol% (2.2 wt%). This product yield and composition represent 1090 ethylene turnovers and 8 methyl acrylate turnovers. Gel permeation chromatography (trichlorobenzene,  $135^{\circ}\text{C}$ , polystyrene reference, results calculated as polyethylene using universal calibration theory):  $M_n=362$ ;  $M_w=908$ ;  $M_w/M_n=2.51$ .

#### Example 104

A 53-mg (0.036-mmol) sample of  $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdCH}_2\text{CH}_2\text{C}(\text{O})\text{CH}_3\}\text{BAF}^+$  was placed in a 600-mL Parr® stirred autoclave under nitrogen. To this was added 100 mL of dry, deaerated methylene chloride. The autoclave was immersed in a cool water bath and stirred

as it was pressurized to 4.8 MPa with ethylene.  
Ethylene was continuously fed with stirring at 4.8 MPa and 23°C for 23 hr; the ethylene then was vented. The product consisted of a clear rubber, slightly swollen with methylene chloride. The polymer was dried under high vacuum at room temperature to yield 34.5 g (34,100 catalyst turnovers) of clear rubbery polyethylene. <sup>1</sup>H NMR analysis (CDCl<sub>3</sub>): 110 methyl carbons per 1000 methylene carbons. Gel permeation chromatography (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal calibration theory): M<sub>n</sub>=243,000; M<sub>w</sub>=676,000; M<sub>w</sub>/M<sub>n</sub>=2.78.

#### Example 104

A 83-mg (0.056-mmol) sample of {[(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>]PdCH<sub>2</sub>CH<sub>2</sub>C(O)CH<sub>3</sub>}BAF<sup>-</sup> was placed in a 600-mL Parr® stirred autoclave under nitrogen. To this was added 70 mL of dry, deaerated, ethanol-free chloroform. The autoclave was immersed in a cool water bath and stirred as it was pressurized to 4.7 MPa with ethylene. Ethylene was continuously fed with stirring at 4.7 MPa and 23°C for 21 hr; the ethylene then was vented. The product consisted of a pink, rubbery, foamed polyethylene, slightly swollen with chloroform. The polymer was dried under vacuum at 40°C to yield 70.2 g (44,400 catalyst turnovers) of pink, rubbery polyethylene which was slightly tacky. <sup>1</sup>H NMR analysis (CDCl<sub>3</sub>): 111 methyl carbons per 1000 methylene carbons. Gel permeation chromatography (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal calibration theory): M<sub>n</sub>=213,000; M<sub>w</sub>=728,000; M<sub>w</sub>/M<sub>n</sub>=3.41.

#### Example 105

A 44-mg (0.052-mmol) sample of {[(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>]PdCH<sub>2</sub>CH<sub>2</sub>C(O)CH<sub>3</sub>}SbF<sub>6</sub><sup>-</sup> was magnetically stirred under nitrogen in a 50-mL Schlenk flask with 20 mL of dry, deaerated methylene chloride. To this was added 5 mL (5.25 g; 73 mmol) of freshly distilled



acrylic acid (contains a few ppm of phenothiazine as a radical polymerization inhibitor) via syringe and the mixture was immediately pressurized with ethylene at 5.52 kPa and stirred for 40 hr. The dark yellow solution was rotary evaporated and the residue was stirred with 50 mL water for 15 min to extract any acrylic acid homopolymer. The water was drawn off with a pipette and rotary evaporated to yield 50 mg of dark residue. The polymer which had been water-extracted was heated under high vacuum to yield 1.30 g of ethylene/acrylic acid copolymer as a dark brown oil. The infrared spectrum showed strong COOH absorbances at 3400-2500 and at  $1705\text{cm}^{-1}$ , as well as strong methylene absorbances at 3000-2900 and  $1470\text{cm}^{-1}$ .

A 0.2-g sample of the ethylene/acrylic acid copolymer was treated with diazomethane in ether to esterify the COOH groups and produce an ethylene/methyl acrylate copolymer. The infrared spectrum of the esterified copolymer showed a strong ester carbonyl absorbance at  $1750\text{cm}^{-1}$ ; the COOH absorbances were gone.  $^1\text{H}$  NMR analysis ( $\text{CDCl}_3$ ): 87 methyl carbons per 1000 methylene carbons. Comparison of the integrals of the ester methoxy (3.67ppm) and ester methylene ( $\text{CH}_2\text{COOMe}$ ; 2.30ppm) peaks with the integrals of the carbon chain methyls (0.8-0.9ppm) and methylenes (1.2-1.3ppm) indicated a methyl acrylate content of 5.3 mol% (14.7 wt% methyl acrylate  $\Rightarrow$  12.3 wt% acrylic acid in the original copolymer). This product yield and composition represent 780 ethylene turnovers and 43 acrylic acid turnovers. Gel permeation chromatography (tetrahydrofuran,  $30^\circ\text{C}$ , polymethylmethacrylate reference, results calculated as polymethylmethacrylate using universal calibration theory):  $M_n=25,000$ ;  $M_w=42,800$ ;  $M_w/M_n=1.71$ .

Listed below are the  $^{13}\text{C}$  NMR data upon which the above analysis is based.

$^{13}\text{C}$  NMR Data  
 $\text{CDCl}_3$ , 0.05M CrAcAc,  $30^\circ\text{C}$

Freq ppm	Intensity
----------	-----------

51.0145	24.9141	
45.434	1.11477	MEB <sub>0</sub>
38.8925	2.29147	
38.5156	6.51271	
37.3899	10.7484	
37.0713	17.3903	
36.7634	17.6341	
36.4182	3.57537	
36.2961	6.0822	
34.459	2.158	
34.0289	9.49713	
33.7369	34.4456	
33.3705	49.2646	
32.8926	18.2918	
32.3935	10.5014	
32.0271	3.5697	3B <sub>5</sub>
31.5705	30.6837	3B <sub>6</sub> +, 3EOC
31.1723	1.54526	
29.813	46.4503	
29.3511	117.987	
29.1387	21.034	
28.9953	30.603	
28.613	7.18386	
27.2007	8.02265	
26.744	23.8731	
26.3777	46.8498	
26.006	5.42389	
25.5547	8.13592	
25.0609	5.46013	2 EB <sub>4</sub> (tentative)
24.9175	2.30355	2 EB <sub>4</sub> (tentative)
24.6042	15.7434	2 EB <sub>5</sub> +
23.7547	2.78914	
23.3777	5.63727	
22.7936	8.07071	2B <sub>4</sub>
22.6768	3.78032	2B <sub>4</sub>
22.3211	33.1603	2B <sub>5</sub> +, 2EOC
19.3477	15.4369	1B <sub>1</sub>
18.8645	5.97477	1B <sub>1</sub>
14.1814	1.99297	1B <sub>3</sub>
13.7407	38.5361	1B <sub>4</sub> +, 1EOC
11.0274	6.19758	1B <sub>2</sub>
10.5124	10.4707	1B <sub>2</sub>
176.567	9.61122	EB <sub>0</sub> carbonyl
174.05	9.03673	EB <sub>1</sub> + carbonyl
173.779	85.021	EB <sub>1</sub> + carbonyl

Example 106

A 25-mg (0.029-mmol) sample of  $\{[(2,6-i-PrPh)_2DABMe_2]PdCH_2CH_2C(O)CH_3\}SbF_6^-$  was magnetically stirred under 55.2 kPa of ethylene in a 50-mL Schlenk flask with 20 mL of dry methylene chloride and 5 mL (4.5 g; 39 mmol) of methyl 4-pentenoate for 40 hr at room temperature. The yellow solution was rotary

evaporated to yield 3.41 g of ethylene/methyl 4-pentenoate copolymer as a yellow oil. The infrared spectrum of the copolymer showed a strong ester carbonyl absorbance at  $1750\text{cm}^{-1}$ .  $^1\text{H}$  NMR analysis (CDCl<sub>3</sub>): 84 methyl carbons per 1000 methylene carbons. Comparison of the integrals of the ester methoxy (3.67ppm) and ester methylene (CH<sub>2</sub>COOMe; 2.30ppm) peaks with the integrals of the carbon chain methyls (0.8-0.9ppm) and methylenes (1.2-1.3ppm) indicated a methyl 4-pentenoate content of 6 mol% (20 wt%). This yield and composition represent about 3400 ethylene turnovers and 200 methyl 4-pentenoate turnovers.  $^{13}\text{C}$  NMR quantitative analysis: branching per 1000 CH<sub>2</sub>: total Methyls (93.3), Methyl (37.7), Ethyl (18.7), Propyl (2), Butyl (8.6), ≥Am and end of chains (26.6), ≥Bu and end of chains (34.8); ester-bearing branches -CH(CH<sub>2</sub>)<sub>n</sub>CO<sub>2</sub>CH<sub>3</sub> as a % of total ester: n≥5 (38.9), n=4 (8.3), n=1,2,3 (46.8), n=0 (6); chemical shifts were referenced to the solvent: chloroform-d<sub>1</sub> (77 ppm). Gel permeation chromatography (tetrahydrofuran, 30°C, polymethylmethacrylate reference, results calculated as polymethylmethacrylate using universal calibration theory):  $M_n=32,400$ ;  $M_w=52,500$ ;  $M_w/M_n=1.62$ .

#### Example 107

A 21-mg (0.025-mmol) sample of  $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdCH}_2\text{CH}_2\text{C}(\text{O})\text{CH}_3\}\text{SbF}_6^-$  was magnetically stirred under nitrogen in a 50-mL Schlenk flask with 5 mL of dry methylene chloride and 5 mL (4.5 g; 39 mmol) of methyl 4-pentenoate for 74 hr. The yellow solution was rotary evaporated to yield 0.09 g of a yellow oil, poly[methyl 4-pentenoate]. The infrared spectrum showed a strong ester carbonyl absorbance at  $1750\text{cm}^{-1}$ . The  $^1\text{H}$  NMR (CDCl<sub>3</sub>) spectrum showed olefinic protons at 5.4-5.5ppm; comparing the olefin integral with the integral of the ester methoxy at 3.67ppm indicates an average degree of polymerization of 4 to 5. This example demonstrates the ability of this catalyst to

homopolymerize alpha olefins bearing polar functional groups not conjugated to the carbon-carbon double bond.

Example 108

A 53-mg (0.063-mmol) sample of  $\{[(2,6-i-PrPh)_2DABMe_2]PdCH_2CH_2C(O)CH_3\}SbF_6^-$  was placed in a 600-mL Parr® stirred autoclave under nitrogen. To this was added 25 mL of dry, deaerated toluene and 25 mL (26 g; 0.36 mol) of freshly distilled acrylic acid containing about 100 ppm phenothiazine. The autoclave was pressurized to 2.1 MPa with ethylene and was stirred for 68 hr at 23°C; the ethylene was then vented. The autoclave contained a colorless, hazy solution. The solution was rotary evaporated and the concentrate was taken up in 50 mL of chloroform, filtered through diatomaceous earth, rotary evaporated, and then held under high vacuum to yield 2.23 g of light brown, very viscous liquid ethylene/acrylic acid copolymer. The infrared spectrum showed strong COOH absorbances at 3400-2500 and at 1705cm<sup>-1</sup>, as well as strong methylene absorbances at 3000-2900 and 1470cm<sup>-1</sup>.

A 0.3-g sample of the ethylene/acrylic acid copolymer was treated with diazomethane in ether to esterify the COOH groups and produce an ethylene/methyl acrylate copolymer. The infrared spectrum showed a strong ester carbonyl absorbance at 1750cm<sup>-1</sup>; the COOH absorbances were gone. <sup>1</sup>H NMR analysis (CDCl<sub>3</sub>): 96 methyl carbons per 1000 methylene carbons. Comparison of the integrals of the ester methoxy (3.67ppm) and ester methylene (CH<sub>2</sub>COOMe; 2.30ppm) peaks with the integrals of the carbon chain methyls (0.8-0.9ppm) and methylenes (1.2-1.3ppm) indicated a methyl acrylate content of 1.8 mol% (5.4 wt% methyl acrylate => 4.5 wt% acrylic acid in the original copolymer). This product yield and composition represent 1200 ethylene turnovers and 22 acrylic acid turnovers. Gel permeation chromatography (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using

universal calibration theory):  $M_n=5,330$ ;  $M_w=15,000$ ;  
 $M_w/M_n=2.82$ .

#### Example 109

A 600-mL stirred Parr® autoclave was sealed and  
5 flushed with nitrogen. Fifty mL (48 g; 0.56 mol) of  
dry, deaerated methyl acrylate was introduced into the  
autoclave via gas tight syringe through a port on the  
autoclave head. Then 60 mg (0.07 mmol) of  $\{[(2,6-i-PrPh)_2DABMe_2]PdMe(Et_2O)\}BAF^-$  was introduced into the  
10 autoclave in the following manner: a 2.5-mL gas tight  
syringe with a syringe valve was loaded with 60 mg of  
 $\{[(2,6-i-PrPh)_2DABMe_2]PdMe(Et_2O)\}BAF^-$  under nitrogen in  
a glove box; then 1 mL of dry, deaerated methylene  
chloride was drawn up into the syringe and the contents  
15 were quickly injected into the autoclave through a head  
port. This method avoids having the catalyst in  
solution with no stabilizing ligands.

The autoclave body was immersed in a running tap  
water bath; the internal temperature was very steady at  
20 22°C. The autoclave was pressurized with ethylene to  
2.8 MPa and continuously fed ethylene with stirring for  
4.5 hr. The ethylene was then vented and the product,  
a mixture of methyl acrylate and yellow gooey polymer,  
was rinsed out of the autoclave with chloroform, rotary  
25 evaporated, and held under high vacuum overnight to  
yield 4.2 g of thick, light-brown liquid  
ethylene/methyl acrylate copolymer. The infrared  
spectrum of the product exhibited a strong ester  
carbonyl stretch at  $1740cm^{-1}$ .  $^1H$  NMR analysis ( $CDCl_3$ ):  
30 82 methyl carbons per 1000 methylene carbons.  
Comparison of the integrals of the ester methoxy  
(3.67ppm) and ester methylene ( $CH_2COOMe$ ; 2.30ppm) peaks  
with the integrals of the carbon chain methyls (0.8-  
0.9ppm) and methylenes (1.2-1.3ppm) indicated a methyl  
35 acrylate content of 1.5 mol% (4.4 wt%). This product  
yield and composition represent 2000 ethylene turnovers  
and 31 methyl acrylate turnovers.  $^{13}C$  NMR analysis:  
branching per 1000  $CH_2$ : total Methyls (84.6), Methyl

(28.7), Ethyl (15.5), Propyl (3.3), Butyl (8.2), 2Hex -  
and End Of Chain (23.9), methyl acrylate (13.9). Ester-  
bearing  $-\text{CH}(\text{CH}_2)_n\text{CO}_2\text{CH}_3$  branches as a % of total ester:  
n $\geq$ 5 (34.4), n=4 (6.2), n=1,2,3 (13), n=0 (46.4). Mole%:  
5 ethylene (97.6), methyl acrylate (2.4); chemical shifts  
were referenced to the solvent: the high field carbon  
of 1,2,4-trichlorobenzene (127.8 ppm). Gel permeation  
chromatography (tetrahydrofuran, 30°C,  
polymethylmethacrylate reference, results calculated as  
10 polymethylmethacrylate using universal calibration  
theory):  $M_n=22,000$ ;  $M_w=45,500$ ;  $M_w/M_n=2.07$ .

A mixture of 1.45 g of this ethylene/methyl  
acrylate copolymer, 20 mL dioxane, 2 mL water, and 1  
mL of 50% aqueous NaOH was magnetically stirred at  
15 reflux under nitrogen for 4.5 hr. The liquid was then  
decanted away from the swollen polymer and the polymer  
was stirred several hours with three changes of boiling  
water. The polymer was filtered, washed with water and  
methanol, and dried under vacuum (80°C/nitrogen purge)  
20 to yield 1.2 g soft of ionomer rubber, insoluble in hot  
chloroform. The FTIR-ATR spectrum of a pressed film  
(pressed at 125°C/6.9 MPa) showed a strong ionomer peak  
at  $1570\text{cm}^{-1}$  and virtually no ester carbonyl at  $1750\text{cm}^{-1}$ .  
The pressed film was a soft, slightly tacky rubber  
25 with about a 50% elongation to break. This example  
demonstrates the preparation of an ionomer from this  
ethylene/methyl acrylate polymer.

#### Example 110

The complex  $[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdMeCl}$  (0.020 g,  
30 0.036 mmol) was weighed into a vial and dissolved in 6  
ml  $\text{CH}_2\text{Cl}_2$ . NaBAF (0.032g, 0.036 mmol) was rinsed into  
the stirring mixture with 4 ml of  $\text{CH}_2\text{Cl}_2$ . There was an  
immediate color change from orange to yellow. The  
solution was stirred under 6.2 MPa ethylene in a Fisher  
35 Porter tube with temperature control at 19°C. The  
internal temperature rose to 22°C during the first 15  
minutes. The temperature controller was raised to  
30°C. After 35 minutes, the reaction was consuming

ethylene slowly. After a total reaction time of about 20 h, there was no longer detectable ethylene consumption, but the liquid level in the tube was noticeably higher. Workup by addition to excess MeOH gave a viscous liquid precipitate. The precipitate was redissolved in  $\text{CH}_2\text{Cl}_2$ , filtered through a 0.5 micron PTFE filter and reprecipitated by addition to excess MeOH to give 7.208 g dark brown viscous oil (7180 equivalents of ethylene per Pd).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 0.8-1.0 (m,  $\text{CH}_3$ ); 1.0-1.5 (m, CH and  $\text{CH}_2$ ). Integration allows calculation of branching: 118 methyl carbons per 1000 methylene carbons. GPC in THF vs. PMMA standard:  $M_n=12,700$ ,  $M_w=28,800$ ,  $M_w/M_n=2.26$ .

#### Example 111

The solid complex  $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdMe}(\text{Et}_2\text{O})\}\text{SbF}_6^-$  (0.080 g, 0.096 mmol) was placed in a Schlenk flask which was evacuated and refilled with ethylene twice. Under one atm of ethylene, black spots formed in the center of the solid complex and grew outward as ethylene was polymerized in the solid state and the resulting exotherm destroyed the complex. Solid continued to form on the solid catalyst that had not been destroyed by the exotherm, and the next day the flask contained considerable solid and the reaction was still slowly consuming ethylene. The ethylene was disconnected and 1.808 g of light gray elastic solid was removed from the flask (644 equivalents ethylene per Pd). The  $^1\text{H}$  NMR in  $\text{CDCl}_3$  was similar to example 110 with 101 methyl carbons per 1000 methylene carbons. Differential Scanning Calorimetry (DSC): first heat 25 to  $150^\circ\text{C}$ ,  $15^\circ\text{C}/\text{min}$ , no events; second heat  $-150$  to  $150^\circ\text{C}$ ,  $T_g = -53^\circ\text{C}$  with an endothermic peak centered at  $-20^\circ\text{C}$ ; third heat  $-150$  to  $275^\circ\text{C}$ ,  $T_g = -51^\circ\text{C}$  with an endothermic peak centered at  $-20^\circ\text{C}$ . GPC (trichlorobenzene,  $135^\circ\text{C}$ , polystyrene reference, results calculated as linear polyethylene using universal calibration theory):  $M_n=13,000$ .  $M_w=313,000$   $M_w/M_n=24$ .

Example 11

The complex  $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdMe}(\text{Et}_2\text{O})\}\text{SbF}_6^-$  (0.084 g, 0.100 mmol) was loaded into a Schlenk flask in the drybox followed by 40 ml of dry dioxane. The septum-capped flask was connected to a Schlenk line and the flask was then briefly evacuated and refilled with ethylene. The light orange mixture was stirred under an ethylene atmosphere at slightly above 1 atm by using a mercury bubbler. There was rapid uptake of ethylene. A room temperature water bath was used to control the temperature of the reaction. After 20 h, the reaction was worked up by removing the solvent in vacuo to give 10.9 g of a highly viscous fluid (3870 equivalents of ethylene per Pd). Dioxane is a solvent for the Pd complex and a non-solvent for the polymer product.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 0.8-1.0 (m,  $\text{CH}_3$ ); 1.0-1.5 (m, CH and  $\text{CH}_2$ ). Integration allows calculation of branching: 100 methyl carbons per 1000 methylene carbons. GPC (trichlorobenzene,  $135^\circ\text{C}$ , polystyrene reference, results calculated as linear polyethylene using universal calibration theory): Partially resolved trimodal distribution with  $M_n=16300$ ,  $M_w=151000$ ,  $M_w/M_n=9.25$ . DSC (second heat,  $-150^\circ\text{C}$  to  $150^\circ\text{C}$ ,  $15^\circ\text{C}/\text{min}$ )  $T_g=-63^\circ\text{C}$ , endothermic peak centered at  $-30^\circ\text{C}$ .

Example 112

Polymerization of ethylene was carried out according to example 112, using pentane as solvent. Pentane is a non-solvent for the Pd complex and a solvent for the polymer product. The reaction gave 7.47 g of dark highly viscous fluid (2664 equivalents of ethylene per Pd).  $^1\text{H}$  NMR analysis ( $\text{CDCl}_3$ ): 126 methyl carbons per 1000 methylene carbons.  $^{13}\text{C}$  NMR analysis, branching per 1000  $\text{CH}_2$ : Total methyls (128.8), Methyl (37.8), Ethyl (27.2), Propyl (3.5), Butyl (14.5), Amyl (2.5),  $\geq\text{Hexyl}$  and end of chain (44.7), average number of carbon atoms for  $\geq\text{Hexyl}$  branches = 16.6 (calculated from intrinsic viscosity



and GPC molecular weight data). Quantitation of the -  
CH<sub>2</sub>CH(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>3</sub> structure per 1000 CH<sub>2</sub>'s: 8.3. These  
side chains are counted as a Methyl branch and an Ethyl  
branch in the quantitative branching analysis. GPC  
5 (trichlorobenzene, 135°C, polystyrene reference,  
results calculated as linear polyethylene using  
universal calibration theory):  $M_n=9,800$ ,  $M_w=16,100$ ,  
 $M_w/M_n=1.64$ . Intrinsic viscosity (trichlorobenzene,  
135°C) = 0.125 g/dL. Absolute molecular weights  
10 calculated by GPC (trichlorobenzene, 135°C, polystyrene  
reference, corrected for branching using measured  
intrinsic viscosity):  $M_n=34,900$ ,  $M_w=58,800$ ,  $M_w/M_n=1.68$ .  
DSC (second heat, -150°C to 150°C, 15°C/min)  $T_g = -$   
71°C, endothermic peak centered at -43 °C.

15 Example 114

Polymerization of ethylene was carried out  
according to example 112, using distilled degassed  
water as the medium. Water is a non-solvent for both  
the Pd complex and the polymer product. The mixture  
20 was worked up by decanting the water from the product  
which was then dried in vacuo to give 0.427 g of dark  
sticky solid (152 equivalents of ethylene per Pd). <sup>1</sup>H  
NMR analysis (CDCl<sub>3</sub>): 97 methyl carbons per 1000  
methylene carbons. GPC (trichlorobenzene, 135°C,  
25 polystyrene reference, results calculated as linear  
polyethylene using universal calibration theory):  
 $M_n=25,100$ ,  $M_w=208,000$ ,  $M_w/M_n=8.31$ .

Example 115

Polymerization of ethylene was carried out  
30 according to example 112, using 2-ethylhexanol as the  
solvent. The Pd complex is sparingly soluble in this  
solvent and the polymer product is insoluble. The  
polymer product formed small dark particles of high  
viscosity liquid suspended in the 2-ethylhexanol. The  
35 solvent was decanted and the polymer was dissolved in  
CHCl<sub>3</sub> and reprecipitated by addition of excess MeOH.  
The solvent was decanted, and the reprecipitated  
polymer was dried in vacuo to give 1.66 g of a dark

highly viscous fluid (591 equivalents of ethylene per Pd).  $^1\text{H}$  NMR analysis ( $\text{CDCl}_3$ ): 122 methyl carbons per 1000 methylene carbons. GPC (trichlorobenzene,  $135^\circ\text{C}$ , polystyrene reference, results calculated as linear polyethylene using universal calibration theory):  
5  $M_n=7,890$ ,  $M_w=21,600$ ,  $M_w/M_n=2.74$ .

Example 116

The solid complex  $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdMe}(\text{Et}_2\text{O})\}\text{SbF}_6^-$  (0.084 g, 0.100 mmol) was  
10 loaded into a Schlenk flask in the drybox. The flask was connected to a Schlenk line under 1 atm of ethylene, and cooled to  $-78^\circ\text{C}$ . Solvent, ( $\text{CH}_2\text{Cl}_2$ , 40 ml) was added by syringe and after equilibrating at  $-78^\circ\text{C}$  under ethylene, the mixture was warmed to room  
15 temperature under ethylene. The mixture was stirred under an ethylene atmosphere at slightly above 1 atm by using a mercury bubbler. There was rapid uptake of ethylene. A room temperature water bath was used to control the temperature of the reaction. After 24 h,  
20 the reaction was worked up by removing the solvent in vacuo to give 24.5 g of a highly viscous fluid (8730 equivalents of ethylene per Pd).  $\text{CH}_2\text{Cl}_2$  is a good solvent for both the Pd complex and the polymer product. The polymer was dissolved in  $\text{CH}_2\text{Cl}_2$ , and  
25 reprecipitated by addition to excess MeOH in a tared flask. The solvent was decanted, and the reprecipitated polymer was dried in vacuo to give 21.3 g of a dark highly viscous fluid.  $^1\text{H}$  NMR analysis ( $\text{CDCl}_3$ ): 105 methyl carbons per 1000 methylene carbons.  
30 C-13 NMR analysis, branching per 1000  $\text{CH}_2$ : Total methyls (118.6), Methyl (36.2), Ethyl (25.9), Propyl (2.9), Butyl (11.9), Amyl (1.7),  $\geq$ Hexyl and end of chains (34.4), average number of carbon atoms for  $\geq$  Hexyl branches = 22.5 (calculated from intrinsic  
35 viscosity and GPC molecular weight data). Quantitation of the  $-\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$  structure per 1000  $\text{CH}_2$ 's: 8.1. These side chains also counted as a Methyl branch and an Ethyl branch in the quantitative branching analysis.

- GPC (trichlorobenzene, 135°C, polystyrene reference, results calculated as linear polyethylene using universal calibration theory):  $M_n=25,800$ ,  $M_w=45,900$ ,  $M_w/M_n=1.78$ . Intrinsic viscosity (trichlorobenzene, 135°C) = 0.24 g/dL. Absolute molecular weights calculated by GPC (trichlorobenzene, 135°C, polystyrene reference, corrected for branching using measured intrinsic viscosity):  $M_n=104,000$ ,  $M_w=188,000$ ,  $M_w/M_n=1.81$ .
- 10 Listed below are the  $^{13}\text{C}$  NMR data upon which the above analysis is based.

<sup>13</sup>C NMR Data  
TCB, 120C, 0.06M CrAcAc

Freq ppm	Intensity	
39.7233	5.12305	
39.318	17.6892	MB <sub>2</sub>
38.2022	17.9361	MB <sub>3</sub> +
37.8369	32.3419	MB <sub>3</sub> +
37.2469	43.1136	αB <sub>1</sub> , 3B <sub>3</sub>
36.8335	10.1653	αB <sub>1</sub> , 3B <sub>3</sub>
36.7452	14.674	αB <sub>1</sub> , 3B <sub>3</sub>
34.9592	10.3554	αγ+B, (4B <sub>4</sub> , 5B <sub>5</sub> , etc.)
34.6702	24.015	αγ+B, (4B <sub>4</sub> , 5B <sub>5</sub> , etc.)
34.5257	39.9342	αγ+B, (4B <sub>4</sub> , 5B <sub>5</sub> , etc.)
34.2006	109.158	αγ+B, (4B <sub>4</sub> , 5B <sub>5</sub> , etc.)
33.723	36.1658	αγ+B, (4B <sub>4</sub> , 5B <sub>5</sub> , etc.)
33.3136	12.0398	MB <sub>1</sub>
32.9323	20.7242	MB <sub>1</sub>
32.4266	6.47794	3B <sub>5</sub>
31.9409	96.9874	3B <sub>6</sub> +, 3EOC
31.359	15.2429	γ+γ+B, 3B <sub>4</sub>
31.0981	19.2981	γ+γ+B, 3B <sub>4</sub>
30.6606	15.8689	γ+γ+B, 3B <sub>4</sub>
30.2271	96.7986	γ+γ+B, 3B <sub>4</sub>
30.1188	54.949	γ+γ+B, 3B <sub>4</sub>
29.7455	307.576	γ+γ+B, 3B <sub>4</sub>
29.5809	36.2391	γ+γ+B, 3B <sub>4</sub>
29.3361	79.3542	γ+γ+B, 3B <sub>4</sub>
29.2157	23.0783	γ+γ+B, 3B <sub>4</sub>
27.6424	24.2024	βγ+B, 2B <sub>2</sub> , (4B <sub>5</sub> , etc.)
27.526	29.8995	βγ+B, 2B <sub>2</sub> , (4B <sub>5</sub> , etc.)
27.3534	23.1626	βγ+B, 2B <sub>2</sub> , (4B <sub>5</sub> , etc.)
27.1607	70.8066	βγ+B, 2B <sub>2</sub> , (4B <sub>5</sub> , etc.)
27.0042	109.892	βγ+B, 2B <sub>2</sub> , (4B <sub>5</sub> , etc.)
26.5908	7.13232	βγ+B, 2B <sub>2</sub> , (4B <sub>5</sub> , etc.)
26.3941	23.945	βγ+B, 2B <sub>2</sub> , (4B <sub>5</sub> , etc.)
25.9446	4.45077	βγ+B, 2B <sub>2</sub> , (4B <sub>5</sub> , etc.)
24.4034	9.52585	ββB
24.2428	11.1161	ββB
23.1391	21.2608	2B <sub>4</sub>
23.0227	11.2909	2B <sub>4</sub>
22.6494	103.069	2B <sub>5</sub> +, 2EOC
20.0526	5.13224	2B <sub>3</sub>
19.7355	37.8832	1B <sub>1</sub>
19.2017	14.8043	1B <sub>1</sub> , Structure XXVII
14.4175	4.50604	1B <sub>3</sub>
13.9118	116.163	1B <sub>4</sub> +, 1EOC
11.1986	18.5867	1B <sub>2</sub> , Structure XXVII
10.9617	32.3855	1B <sub>2</sub>

Example 117

Polymerization of ethylene was carried out according to example 116, at a reaction temperature of 0°C and reaction time of several hours. The polymer product formed a separate fluid phase on the top of the mixture. The reaction was quenched by adding 2 ml acrylonitrile. The product was moderately viscous fluid, 4.5 g (1600 equivalents of ethylene per Pd). <sup>1</sup>H NMR analysis (CDCl<sub>3</sub>): 108 methyl carbons per 1000 methylene carbons. <sup>13</sup>C NMR analysis, branching per 1000 CH<sub>2</sub>: Total methyls (115.7), Methyl (35.7), Ethyl (24.7), Propyl (2.6), Butyl (11.2), Amyl (3.2), ≥Hexyl and end of chain (37.1). Quantitation of the -CH<sub>2</sub>CH(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>3</sub> structure per 1000 CH<sub>2</sub>'s: 7.0. These side chains are counted as a Methyl branch and an Ethyl branch in the quantitative branching analysis. GPC (trichlorobenzene, 135°C, polystyrene reference, results calculated as linear polyethylene using universal calibration theory: M<sub>n</sub>=15,200, M<sub>w</sub>=23,700, M<sub>w</sub>/M<sub>n</sub>=1.56.

Example 118

The Pd complex {[(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>]PdCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C(O)OCH<sub>3</sub>}SbF<sub>6</sub><sup>-</sup> (0.084 g, 0.100 mmol) was loaded into a Schlenk flask in the drybox, and 40 ml of FC-75 was added. The septum-capped flask was connected to a Schlenk line and the flask was then briefly evacuated and refilled with ethylene from the Schlenk line. The mixture was stirred under an ethylene atmosphere at slightly above 1 atm by using a mercury bubbler. Both the Pd initiator and the polymer are insoluble in FC-75. After 15 days, the reaction flask contained a large amount of gray elastic solid. The FC-75 was decanted, and the solid polymer was then dissolved in CHCl<sub>3</sub> and precipitated by addition of the solution to excess MeOH. The polymer was dried in vacuo, and then dissolved in o-dichlorobenzene at 100°C. The hot solution was filtered through a 10 μm PTFE filter. The filtered polymer solution was shaken

in a separatory funnel with concentrated sulfuric acid, followed by distilled water, followed by 5% NaHCO<sub>3</sub> solution, followed by two water washes. The polymer appeared to be a milky suspension in the organic layer during this treatment. After washing, the polymer was precipitated by addition to excess MeOH in a blender and dried at room temperature in vacuo to give 19.6 g light gray elastic polymer fluff (6980 equivalents of ethylene per Pd). <sup>1</sup>H NMR analysis (CDCl<sub>3</sub>): 112 methyl carbons per 1000 methylene carbons. <sup>13</sup>C NMR analysis, branching per 1000 CH<sub>2</sub>: Total methyls (114.2), Methyl (42.1), Ethyl (24.8), Propyl (5.1), Butyl (10.2), Amyl (4), ≥Hexyl and end of chain (30.3), average number of carbon atoms for ≥Hexyl branches = 14.4 (calculated from intrinsic viscosity and GPC molecular weight data). GPC (trichlorobenzene, 135°C, polystyrene reference, results calculated as linear polyethylene using universal calibration theory: M<sub>n</sub>=110,000, M<sub>w</sub>=265,000, M<sub>w</sub>/M<sub>n</sub>=2.40. Intrinsic viscosity (trichlorobenzene, 135°C) = 1.75 g/dL. Absolute molecular weights calculated by GPC (trichlorobenzene, 135°C, polystyrene reference, corrected for branching using measured intrinsic viscosity): M<sub>n</sub>=214,000, M<sub>w</sub>=535,000, M<sub>w</sub>/M<sub>n</sub>=2.51.

25

Example 119

Polymerization of ethylene was carried out according to example 112, using the complex {[(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>]PdCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C(O)OCH<sub>3</sub>}SbF<sub>6</sub><sup>-</sup> (0.084 g, 0.100 mmol) as the initiator and CHCl<sub>3</sub> as the solvent. The reaction gave 28.4 g of dark viscous fluid (10,140 equivalents of ethylene per Pd). <sup>1</sup>H NMR analysis (CDCl<sub>3</sub>): 108 methyl carbons per 1000 methylene carbons. <sup>13</sup>C NMR analysis, branching per 1000 CH<sub>2</sub>: Total methyls (119.5), Methyl (36.9), Ethyl (25.9), Propyl (2.1), Butyl (11), Amyl (1.9), ≥Hexyl and end of chain (38.9). GPC (trichlorobenzene, 135°C, polystyrene reference, results calculated as linear polyethylene

using universal calibration theory):  $M_n=10,800$ ,  
 $M_w=26,800$ ,  $M_w/M_n=2.47$ .

#### Example 120

Polymerization of ethylene was carried out  
 5 according to example 112, using the complex  $\{[(2,6\text{-}i\text{-PrPh})_2\text{DABMe}_2]\text{PdMe}(\text{OSO}_2\text{CF}_3)\}$  (0.068g, 0.10 mmol) as the  
 initiator and  $\text{CHCl}_3$  as the solvent. The reaction gave  
 5.98 g of low viscosity fluid (2130 equivalents of  
 ethylene per Pd).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 0.8-1.0 (m,  $\text{CH}_3$ );  
 10 1.0-1.5 (m, CH and  $\text{CH}_2$ ); 1.5-1.7 (m,  $\text{CH}_3\text{CH}=\text{CH}-$ ); 1.9-  
 2.1 (broad,  $-\text{CH}_2\text{CH}=\text{CHCH}_2-$ ); 5.3-5.5 (m,  $-\text{CH}=\text{CH}-$ ).  
 Integration of the olefin end groups assuming one  
 olefin per chain gives  $M_n = 630$  ( $\text{DP} = 24$ ). A linear  
 polymer with this molecular weight and methyl groups at  
 15 both ends should have 46 methyl carbons per 1000  
 methylene carbons. The value measured by integration  
 is 161, thus this polymer is highly branched.

#### Example 121

Polymerization of ethylene was carried out  
 20 according to example 112, using the complex  $\{[(2,6\text{-}i\text{-PrPh})_2\text{DABH}_2]\text{PdCH}_2\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OCH}_3\}\text{SbF}_6^-$  (0.082 g, 0.10 mmol)  
 as the initiator and  $\text{CHCl}_3$  as the solvent. The  
 reaction gave 4.47 g of low viscosity fluid (1600  
 equivalents of ethylene per Pd).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) is  
 25 similar to example 120. Integration of the olefin end  
 groups assuming one olefin per chain gives  $M_n = 880$  ( $\text{DP}$   
 $= 31$ ). A linear polymer with this molecular weight and  
 methyl groups at both ends should have 34 methyl  
 carbons per 1000 methylene carbons. The value measured  
 30 by integration is 156, thus this polymer is highly  
 branched.

#### Example 122

Polymerization of ethylene was carried out  
 according to example 112, using the complex  $\{[(2,6\text{-}i\text{-PrPh})_2\text{DABMe}_2]\text{PdCH}_2\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OCH}_3\}\text{BCl}(\text{C}_6\text{F}_5)_3^-$  (0.116 g,  
 35 0.10 mmol) as the initiator and  $\text{CHCl}_3$  as the solvent.  
 The reaction gave 0.278 g of low viscosity fluid, after  
 correcting for the catalyst residue this is 0.160 g (57

equivalents of ethylene per Pd).  $M_n$  estimated by integration of olefin end groups is 300.

Example 123

The complex  $[(2,6-i-PrPh)_2DABMe_2]PdMeCl$  (0.056 g, 0.10 mmol) was loaded into a Schlenk flask in the drybox followed by 40 ml of dry toluene. A solution of ethyl aluminum dichloride (1.37 ml of 0.08 M solution in o-dichlorobenzene) was added while stirring. Polymerization of ethylene was carried out using this solution according to example 112. The reaction gave 0.255 g of low viscosity fluid, after correcting for the catalyst residue this is 0.200 g (71 equivalents of ethylene per Pd).  $M_n$  estimated by integration of olefin end groups is 1300.

Example 124

Methyl acrylate was sparged with argon, dried over activated 4A sieves, passed through activity 1 alumina B in the drybox, and inhibited by addition of 20 ppm phenothiazine. The solid complex  $\{[(2,6-i-PrPh)_2DABMe_2]PdMe(Et_2O)\}SbF_6^-$  (0.084 g, 0.100 mmol) was loaded into a Schlenk flask in the drybox. The flask was connected to a Schlenk line under 1 atm of ethylene, and cooled to  $-78^\circ C$ . Forty ml of  $CH_2Cl_2$  was added by syringe and after equilibrating at  $-78^\circ C$  under ethylene, 5 ml of methyl acrylate was added by syringe and the mixture was warmed to room temperature under ethylene. After 40 h, the reaction was worked up by removing the solvent in vacuo to give 3.90 g of moderately viscous fluid. Integration of the  $^1H$  NMR spectrum showed that this copolymer contained 6.9 mole % methyl acrylate. No poly(methyl acrylate) homopolymer could be detected in this sample by  $^1H$  NMR.  $^1H$  NMR shows that a significant fraction of the ester groups are located at the ends of hydrocarbon branches: 3.65(s,  $-CO_2CH_3$ , area=4.5), 2.3(t,  $-CH_2CO_2CH_3$ , ester ended branches, area=3), 1.6(m,  $-CH_2CH_2CO_2CH_3$ , ester ended branches, area=3), 0.95-1.55(m, CH and other  $CH_2$ , area=73), 0.8-0.95(m,  $CH_3$ , ends of branches or ends of



chains, area=9.5) This is confirmed by the  $^{13}\text{C}$  NMR quantitative analysis: Mole%: ethylene (93.1), methyl acrylate (6.9), Branching per 1000  $\text{CH}_2$ : Total methyls (80.2), Methyl (30.1), Ethyl (16.8), Propyl (1.6),  
5 Butyl (6.8), Amyl (1.3),  $\geq$ Hexyl and end of chain (20.1), methyl acrylate (41.3), Ester branches  $\text{CH}(\text{CH}_2)_n\text{CO}_2\text{CH}_3$  as a % of total ester:  $n \geq 5$  (47.8),  $n=4$  (17.4),  $n=1,2,3$  (26.8),  $n=0$  (8).

GPC of this sample was done in THF vs. PMMA  
10 standards using a dual UV/RI detector. The outputs of the two detectors were very similar. Since the UV detector is only sensitive to the ester functionality, and the RI detector is a relatively nonselective mass detector, the matching of the two detector outputs  
15 shows that the ester functionality of the methyl acrylate is distributed throughout the entire molecular weight range of the polymer, consistent with a true copolymer of methyl acrylate and ethylene.

A 0.503 g sample of the copolymer was fractionated  
20 by dissolving in benzene and precipitating partially by slow addition of MeOH. This type of fractionation experiment is a particularly sensitive method for detecting a low molecular weight methyl acrylate rich component since it should be the most soluble material  
25 under the precipitation conditions.

The precipitate 0.349 g, (69%) contained 6.9 mole % methyl acrylate by  $^1\text{H}$  NMR integration, GPC (THF, PMMA standard, RI detector):  $M_n=19,600$ ,  $M_w=29,500$ ,  $M_w/M_n=1.51$ . The soluble fraction 0.180g (36%)  
30 contained 8.3 mole % methyl acrylate by  $^1\text{H}$  NMR integration, GPC (THF, PMMA standard, RI detector):  $M_n=11,700$ ,  $M_w=19,800$ ,  $M_w/M_n=1.70$ . The characterization of the two fractions shows that the acrylate content is only slightly higher at lower  
35 molecular weights. These results are also consistent with a true copolymer of the methyl acrylate with ethylene.

Example 125

Methyl acrylate was sparged with argon, dried over activated 4A sieves, passed through activity 1 alumina B in the drybox, and inhibited by addition of 20 ppm phenothiazine. The complex [(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>]PdMe(OSO<sub>2</sub>CF<sub>3</sub>) (0.068 g, 0.10 mmol) was loaded into a Schlenk flask in the drybox, and 40 ml of CHCl<sub>3</sub> was added followed by 5 ml of methyl acrylate. The septum capped flask was connected to a Schlenk line and the flask was then briefly evacuated and refilled with ethylene from the Schlenk line. The light orange mixture was stirred under an ethylene atmosphere at slightly above 1 atm by using a mercury bubbler. After 20 h, the reaction was worked up by removing the solvent and unreacted methyl acrylate in vacuo to give 1.75 g of a low viscosity copolymer.

<sup>13</sup>C NMR quantitative analysis: Mole%: ethylene (93), methyl acrylate (7), Branching per 1000 CH<sub>2</sub>: Total methyls (100.9), Methyl (33.8), Ethyl (19.8), Propyl (1.9), Butyl (10.1), Amyl (7.3), ≥Hexyl and end of chains (28.4), methyl acrylate (41.8). This sample is low molecular weight - total methyls does not include end of chain methyls. Ester branches - CH(CH<sub>2</sub>)<sub>n</sub>CO<sub>2</sub>CH<sub>3</sub> as a % of total ester: n≥5 (51.3), n=4 (18.4), n=1,2,3 (24), n=0 (6.3).

Example 126

Ethylene and methyl acrylate were copolymerized according to example 125 with catalyst {[(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>]PdCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C(O)OCH<sub>3</sub>}BAF<sup>-</sup> (0.136 g, 0.10 mmol) in CH<sub>2</sub>Cl<sub>2</sub> solvent with a reaction time of 72 hours to give 4.93 g of copolymer.

Example 127

Ethylene and methyl acrylate were copolymerized according to example 125 with catalyst {[(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>]PdCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C(O)OCH<sub>3</sub>}SbF<sub>6</sub><sup>-</sup> (0.084 g, 0.10 mmol) with a reaction time of 72 hours to give 8.19 g of copolymer.

Example 128

Ethylene and methyl acrylate were copolymerized according to example 125 with catalyst  $\{[(2,6\text{-i-PrPh})_2\text{DABH}_2]\text{PdCH}_2\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OCH}_3\}\text{SbF}_6^-$  (0.082 g, 0.10 mmol) to give 1.97 g of copolymer.

Example 129

Ethylene and methyl acrylate were copolymerized according to example 125 with catalyst  $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdMe}(\text{CH}_3\text{CN})\}\text{SbF}_6^-$  (0.080 g, 0.10 mmol) to give 3.42 g of copolymer. The  $^1\text{H}$  NMR shows primarily copolymer, but there is also a small amount of poly(methyl acrylate) homopolymer.

Example 130

Ethylene and methyl acrylate (20 ml) were copolymerized in 20 ml of  $\text{CHCl}_3$  according to example 125 using catalyst  $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdCH}_2\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OCH}_3\}\text{SbF}_6^-$  (0.339 g, 0.40 mmol) to give 2.17 g of copolymer after a reaction time of 72 hours.  $^{13}\text{C}$  NMR quantitative analysis: Mole%: ethylene (76.3), methyl acrylate (23.7). Branching per 1000  $\text{CH}_2$ : Total methyls (28.7), Methyl (20.5), Ethyl (3.8), Propyl (0), Butyl (11),  $\geq$ Amyl and end of chains (13.6), methyl acrylate (138.1). Ester branches -  $\text{CH}(\text{CH}_2)_n\text{CO}_2\text{CH}_3$  as a % of total ester:  $n \geq 5$  (38.8),  $n=4$  (20),  $n=1,2,3$  (15.7),  $n=0$  (25.4).

Example 131

Ethylene and methyl acrylate (20 ml) were copolymerized in 20 ml of  $\text{CHCl}_3$  at  $50^\circ\text{C}$  for 20 hours according to example 125 using catalyst  $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdCH}_2\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OCH}_3\}\text{SbF}_6^-$  (0.339 g, 0.40 mmol) to give 0.795 g of copolymer. DSC (two heats, -150 to  $+150^\circ\text{C}$ ,  $15^\circ\text{C}/\text{min}$ ) shows  $T_g = -48^\circ\text{C}$ .

Example 132

A solution of the ligand  $(2,6\text{-i-PrPh})_2\text{DAB}(\text{Me}_2)$  (0.045 g, 0.11 mmol) dissolved in 2 ml of  $\text{CHCl}_3$  was added to a solution of the complex  $[\text{PdMe}(\text{CH}_3\text{CN})(1,5\text{-cyclooctadiene})]^+\text{SbF}_6^-$  (0.051 g, 0.10 mmol) in 2 ml of  $\text{CHCl}_3$ . This mixture was combined with 35 ml of

additional  $\text{CHCl}_3$  and 5 ml of methyl acrylate in a Schlenk flask in a drybox, and then a copolymerization with ethylene was carried out according to example 125 to give 1.94 g of copolymer.

5

Example 133

Methyl acrylate (5 ml) was added to the solid catalyst  $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdMe}(\text{Et}_2\text{O})\}\text{BF}_4^-$  (0.069g, 0.10 mmol) followed by 40 ml of  $\text{CHCl}_3$ . The addition of methyl acrylate before the  $\text{CHCl}_3$  is often important to avoid deactivation of the catalyst. A copolymerization with ethylene was carried out according to example 125 to give 2.87 g of copolymer.

10

Characterization of poly(ethylene-co-methyl acrylate)  
by  $^1\text{H}$  NMR

15

NMR spectra in  $\text{CDCl}_3$  were integrated and the polymer compositions and branching ratios were calculated. See example 124 for chemical shifts and assignments.

20

Example	Yield(g)	methyl acrylate (mole %)	$\text{CH}_3$ per 1000 $\text{CH}_2$	$\text{CO}_2\text{CH}_3$ per 1000 $\text{CH}_2$
124	3.9	6.9	80	42
125	1.75	7.1	104	45
126	4.93	5.6	87	34
127	8.19	6.1	87	37
128	1.97	7.3	159	50
129	3.42	9.5	86	59
130	2.17	22.8	29	137
131	0.795	41	14	262
132	1.94	6.1	80	36
133	2.87	8.2	70	49

Molecular Weight Characterization

GPC was done in THF using PMMA standards and an RI detector except for example 133 which was done in trichlorobenzene at  $135^\circ\text{C}$  vs. polystyrene reference

25

with results calculated as linear polyethylene using universal calibration theory. When polymer end groups could be detected by  $^1\text{H}$  NMR (5.4 ppm, multiplet, -CH=CH-, internal double bond),  $M_n$  was calculated assuming two olefinic protons per chain.

Example	$M_n$	$M_w$	$M_w/M_n$	$M_n$ ( $^1\text{H}$ NMR)
124	15,500	26,400	1.70	
125	1,540	2,190	1.42	850
126	32,500	49,900	1.54	
127	12,300	22,500	1.83	
128	555	595	1.07	360
129	16,100	24,900	1.55	
130	800	3,180	3.98	1,800
131				1,100
132	15,200	26,000	1.71	
133	5,010	8,740	1.75	

#### Example 134

Ethylene and *t*-butyl acrylate (20 ml) were copolymerized according to example 130 to give 2.039 g of viscous fluid.  $^1\text{H}$  NMR of the crude product showed the desired copolymer along with residual unreacted *t*-butyl acrylate. The weight of polymer corrected for monomer was 1.84 g. The sample was reprecipitated to remove residual monomer by slow addition of excess MeOH to a  $\text{CHCl}_3$  solution. The reprecipitated polymer was dried in vacuo.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 2.2(t,  $-\text{CH}_2\text{CO}_2\text{C}(\text{CH}_3)_3$ , ester ended branches), 1.6(m,  $-\text{CH}_2\text{CH}_2\text{CO}_2\text{C}(\text{CH}_3)_3$ , ester ended branches), 1.45(s,  $-\text{C}(\text{CH}_3)_3$ ), 0.95-1.45(m, CH and other  $\text{CH}_2$ ), 0.75-0.95(m,  $\text{CH}_3$ , ends of hydrocarbon branches or ends of chains). This spectrum shows that the esters are primarily located at the ends of hydrocarbon branches; integration gave 6.7 mole % *t*-butyl acrylate.  $^{13}\text{C}$  NMR quantitative analysis, branching per 1000  $\text{CH}_2$ : Total methyls (74.8), Methyl (27.7), Ethyl (15.3), Propyl (1.5), Butyl (8.6),  $\geq$ Amyl

and end of chains (30.8),  $-\text{CO}_2\text{C}(\text{CH}_3)_3$  ester (43.2).  
 Ester branches  $-\text{CH}(\text{CH}_2)_n\text{CO}_2\text{C}(\text{CH}_3)_3$  as a % of total  
 ester:  $n \geq 5$  (44.3),  $n=1,2,3,4$  (37.2),  $n=0$  (18.5). GPC  
 (THF, PMMA standard):  $M_n=6000$   $M_w=8310$   $M_w/M_n = 1.39$ .

5

Example 135

Glycidyl acrylate was vacuum distilled and  
 inhibited with 50 ppm phenothiazine. Ethylene and  
 glycidyl acrylate (5 ml) were copolymerized according  
 to Example 125 using catalyst  $\{[(2,6\text{-i-}$

10  $\text{PrPh})_2\text{DABMe}_2\}\text{PdCH}_2\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OCH}_3\}\text{SbF}_6^-$  (0.084 g, 0.10  
 mmol). The reaction mixture was filtered through a  
 fritted glass filter to remove chloroform insolubles,  
 and the chloroform was removed *in vacuo* to give 14.1 g  
 viscous yellow oil which still contained residual  
 15 unreacted glycidyl acrylate. The sample was  
 reprecipitated to remove residual monomer by slow  
 addition of excess acetone to a  $\text{CHCl}_3$  solution. The  
 reprecipitated polymer was dried *in vacuo* to give 9.92  
 g of copolymer containing 1.8 mole % glycidyl acrylate.  
 20  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 4.4, 3.9, 3.2, 2.85,  
 2.65 (multiplets, 1H each  $-\text{CH}_2\text{CHCH}_2\text{O}$ ) 2.35 (t,

$-\text{CH}_2\text{CO}_2\text{CH}_2\text{CHCH}_2\text{O}$ , ester ended branches), 1.65(m,

$-\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_2\text{CHCH}_2\text{O}$ , ester ended branches), 0.95-1.5(m, CH

and other  $\text{CH}_2$ ), 0.75-0.95(m,  $\text{CH}_3$ , ends of hydrocarbon  
 25 branches or ends of chains). This spectrum shows that  
 the epoxide ring is intact, and that the glycidyl ester  
 groups are primarily located at the ends of hydrocarbon  
 branches. GPC (THF, PMMA standard):  $M_n=63,100$   
 $M_w=179,000$   $M_w/M_n = 2.85$ .

30  $^{13}\text{C}$  NMR quantitative analysis, branching per 1000  
 $\text{CH}_2$ : Total methyls (101.7), Methyl (32.5), Ethyl  
 (21.3), Propyl (2.4), Butyl (9.5), Amyl (1.4),  $\geq$ Hexyl  
 and end of chains (29.3), Ester branches  $-\text{CH}(\text{CH}_2)_n\text{CO}_2\text{R}$   
 as a % of total ester:  $n \geq 5$  (39.7),  $n=4$  (small amount),  
 35  $n=1,2,3$  (50.7),  $n=0$  (9.6).

A 3.24-g sample of the copolymer was dissolved in 50 mL of refluxing methylene chloride. A solution of 0.18 g oxalic acid dihydrate in 5 mL of 1:1 chloroform-acetone was added to the solution of copolymer and the solvent was evaporated off on a hot plate. The thick liquid was allowed to stand in an aluminum pan at room temperature overnight; the pan was then placed in an oven at 70°C for 1.5 hr followed by 110°C/vacuum for 5 hr. The cured polymer was a dark, non-tacky soft rubber which tore easily (it had a very short elongation to break despite its rubberiness).

#### Example 136

1-Pentene (20 ml) and methyl acrylate (5 ml) were copolymerized in 20 ml chloroform for 96 hours using catalyst  $\{[(2,6\text{-}i\text{-PrPh})_2\text{DABMe}_2]\text{PdCH}_2\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OCH}_3\}\text{SbF}_6$  (0.084 g, 0.10 mmol). The solvent and unreacted monomers were removed in vacuo to give 0.303 g copolymer (0.219 g after correcting for catalyst residue). The  $^1\text{H}$  NMR spectrum was similar to the ethylene/methyl acrylate copolymer of example 124 suggesting that many of the ester groups are located at the ends of hydrocarbon branches. Integration shows that the product contains 21 mole % methyl acrylate. There are 65 acrylates and 96 methylys per 1000 methylene carbons. GPC (THF, PMMA standard):  $M_n=6400$   $M_w=11200$   $M_w/M_n = 1.76$ .

#### Example 137

Benzyl acrylate was passed through activity 1 alumina B, inhibited with 50 ppm phenothiazine, and stored over activated 4A molecular sieves. Ethylene and benzyl acrylate (5 ml) were copolymerized according to example 135 to give 11.32 g of viscous fluid.  $^1\text{H}$  NMR of the crude product showed a mixture of copolymer and unreacted benzyl acrylate (35 wt %). The residual benzyl acrylate was removed by two reprecipitations, the first by addition of excess MeOH to a chloroform solution, and the second by addition of excess acetone to a chloroform solution.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 7.35 (broad

s,  $-\text{CH}_2\text{C}_6\text{H}_5$ ), 5.1(s,  $-\text{CH}_2\text{C}_6\text{H}_5$ ), 2.35(t,  $-\text{CH}_2\text{CO}_2\text{CH}_2\text{C}_6\text{H}_5$ , ester ended branches), 1.6(m,  $-\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_2\text{C}_6\text{H}_5$ , ester ended branches), 0.95-1.5(m, CH and other  $\text{CH}_2$ ), 0.75-0.95(m,  $\text{CH}_3$ , ends of hydrocarbon branches or ends of chains). Integration shows that the product contains 3.7 mole % benzyl acrylate. There are 21 acrylates and 93 methyls per 1000 methylene carbons. GPC (THF, PMMA standard):  $M_n=46,200$   $M_w=73,600$   $M_w/M_n = 1.59$ .

$^{13}\text{C}$  NMR quantitative analysis, Branching per 1000  $\text{CH}_2$ : Total methyls (97.2), Methyl (32.9), Ethyl (20.3), Propyl (2.4), Butyl (9.7), Amyl (2.9),  $\geq$ Hexyl and end of chains (35.2), benzyl acrylate (17.9), Ester branches  $-\text{CH}(\text{CH}_2)_n\text{CO}_2\text{R}$  as a % of total ester:  $n \geq 5$  (44.5),  $n=4$  (7.2),  $n=1,2,3$  (42.3),  $n=0$  (6)

#### Example 138

1-Pentene (10 ml) and ethylene (1 atm) were copolymerized in 30 ml chloroform according to example 125 using catalyst  $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdCH}_2\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OCH}_3\}\text{SbF}_6^-$  (0.084 g, 0.10 mmol) to give 9.11 g highly viscous yellow oil. The  $^1\text{H}$  NMR spectrum was similar to the poly(ethylene) of example 110 with 113 methyl carbons per 1000 methylene carbons.  $^{13}\text{C}$  NMR quantitative analysis, branching per 1000  $\text{CH}_2$ : Total methyls (119.5), Methyl (54.7), Ethyl (16.9), Propyl (8.4), Butyl (7.7), Amyl (7.2),  $\geq$ Hexyl and end of chains (30.9). GPC (trichlorobenzene,  $135^\circ\text{C}$ , polystyrene reference, results calculated as linear polyethylene using universal calibration theory):  $M_n=25,000$ ,  $M_w=44,900$ ,  $M_w/M_n=1.79$ .

Listed below are the  $^{13}\text{C}$  NMR data upon which the above analysis is based.

$^{13}\text{C}$ NMR Data		
TCB, $120^\circ\text{C}$ , 0.05M CrAcAc		
Freq ppm	Intensity	
39.6012	5.53532	
39.4313	6.33425	$\text{MB}_2$
38.3004	8.71403	$\text{MB}_3^+$
37.9446	17.7325	$\text{MB}_3^+$
37.2809	36.416	$\alpha\text{B}_1$ , $3\text{B}_3$
36.7659	5.10586	$\alpha\text{B}_1$ , $3\text{B}_3$



34.3181	56.1758	$\alpha\gamma+B$
33.8243	15.6271	$\alpha\gamma+B$
33.3942	8.09189	$MB_1$
32.9854	20.3523	$MB_1$
32.6721	4.35239	$MB_1$
32.327	4.06305	$3B_5$
31.9394	27.137	$3B_6+, 3 EOC$
31.4031	9.62823	$\gamma+\gamma+B, 3B_4$
30.235	52.8404	$\gamma+\gamma+B, 3B_4$
29.7518	162.791	$\gamma+\gamma+B, 3B_4$
29.3164	26.506	$\gamma+\gamma+B, 3B_4$
27.5695	15.4471	$B\gamma+B, 2B_2$
27.1341	59.1216	$B\gamma+B, 2B_2$
26.4811	8.58222	$B\gamma+B, 2B_2$
24.4475	5.93996	$\beta\beta B$
23.12	5.05181	$2B_4$
22.6369	29.7047	$2B_5+, 2 EOC$
20.1626	6.29481	$2B_3$
19.7378	31.9342	$1B_1$
19.2068	3.93019	$1B_1$
14.2582	5.59441	$1B_3$
13.8706	36.3938	$1B_4+, 1 EOC$
10.9768	9.89028	$1B_2$

Example 139

1-Pentene (20 ml) was polymerized in 20 ml chloroform according to example 138 to give 2.59 g of viscous fluid (369 equivalents 1-pentene per Pd). Integration of the  $^1H$  NMR spectrum showed 118 methyl carbons per 1000 methylene carbons. DSC (two heats, -150 to +150°C, 15°C/min) shows  $T_g = -58^\circ C$  and a low temperature melting endotherm from -50°C to 30°C (32 J/g).

$^{13}C$  NMR quantitative analysis, branching per 1000 CH<sub>2</sub>: Total methyls (118), Methyl (85.3), Ethyl (none detected), Propyl (15.6), Butyl (non detected),  $\geq$  Amyl and end of chains (17.1). GPC (trichlorobenzene, 135°C, polystyrene reference, results calculated as linear polyethylene using universal calibration theory):  $M_n=22,500$ ,  $M_w=43,800$ ,  $M_w/M_n=1.94$ .

Listed below are the  $^{13}C$  NMR data upon which the above analysis is based.

<sup>13</sup>C NMR data

TCB, 120C, 0.05M CrAcAc

<u>Freq ppm</u>	<u>Intensity</u>	
42.6277	4.69744	α for Me & Et <sup>+</sup>
39.5428	9.5323	3 <sup>rd</sup> carbon of a 6 <sup>+</sup> carbon side chain that has a methyl branch at the 4 position
38.1357	3.59535	
37.8384	13.9563	MB <sub>3</sub> <sup>+</sup>
37.5888	28.4579	
37.2224	54.6811	αB <sub>1</sub> , 3B <sub>3</sub>
35.5287	6.51708	
35.2419	3.55603	
34.6366	7.35366	
34.2437	22.3787	
32.911	45.2064	MB <sub>1</sub>
32.5977	10.5375	
32.38	4.02878	
31.8809	14.1607	3B <sub>6</sub> <sup>+</sup> , 3EOC
30.6916	8.44427	γ <sup>+</sup> γ <sup>+</sup> B
30.0703	63.1613	γ <sup>+</sup> γ <sup>+</sup> B
29.6987	248	γ <sup>+</sup> γ <sup>+</sup> B
29.2633	17.9013	γ <sup>+</sup> γ <sup>+</sup> B
28.8916	3.60422	
27.1182	66.2971	βγ <sup>+</sup> B, (4B <sub>5</sub> , etc.)
24.5324	16.8854	
22.5784	16.0395	2B <sub>5</sub> <sup>+</sup> , 2EOC
20.1041	13.2742	
19.6952	54.3903	1B <sub>1</sub> , 2B <sub>3</sub>
14.2104	12.2831	
13.8281	16.8199	1B <sub>4</sub> <sup>+</sup> , EOC, 1B <sub>3</sub>

Integration of the CH<sub>2</sub> peaks due to the structure  
 5 -CH(R)CH<sub>2</sub>CH(R')- , where R is an alkyl group, and R' is  
 an alkyl group with two or more carbons showed that in  
 69% of these structures, R = Me. The region integrated  
 for the structure where both R and R' are ≥Ethyl was  
 39.7 ppm to 41.9 ppm to avoid including an interference  
 10 from another type of methylene carbon on a side chain.

Example 140

[(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>]PdMeCl (0.020 g, 0.036 mmol)  
 was dissolved in 4 ml CH<sub>2</sub>Cl<sub>2</sub> and methyl acrylate  
 15 (0.162 g, 0.38 mmol, inhibited with 50 ppm  
 phenothiazine) was added while stirring. This solution  
 was added to a stirred suspension of NaBAF (0.033 g,  
 0.038 mmol) in 4 ml of CH<sub>2</sub>Cl<sub>2</sub>. After stirring for 1

four, the mixture was filtered through a 0.5  $\mu$ m PTFE membrane filter to remove a flocculant gray precipitate. The solvent was removed from the filtrate in vacuo to give a solid which was recrystallized from a CH<sub>2</sub>Cl<sub>2</sub>/pentane mixture at -40°C to give 0.39 g (75% yield) of orange crystalline  $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdCH}_2\text{CH}_2\text{CH}_2\text{C(O)OCH}_3\}\text{BAF}^-$ . <sup>1</sup>H NMR (CDCl<sub>3</sub>): 0.65(m, CH<sub>2</sub>, 2H); 1.15-1.45(four sets of doublets for -CH(CH<sub>3</sub>)<sub>2</sub> and multiplet at 1.4 for a CH<sub>2</sub>, total area = 26H); 2.19,2.21 (s,s, CH<sub>3</sub> of ligand backbone, 6H); 2.40(m, CH<sub>2</sub>, 2H); 2.90 (m, -CH(CH<sub>3</sub>)<sub>2</sub>, 4H); 3.05(s, -CO<sub>2</sub>CH<sub>3</sub>, 3H); 7.25-7.75(m, aromatic H of ligand and counterion, 19H).

All GPC data reported for examples 141-170, 177, and 204-212 were run in trichlorobenzene vs. polyethylene standards unless otherwise indicated. All DSC data reported for examples 141-170, 177, and 204-212 (second heat, -150°C to 150°, 10 or 15°C/min).

#### Example 141

A Schlenk flask containing  $\{[(2,6\text{-i-PrPh})_2\text{DABH}_2]\text{NiMe(Et}_2\text{O)}\}\text{BAF}^-$  (1.3 mg,  $8.3 \times 10^{-7}$  mol) under an argon atmosphere was cooled to -78°C. Upon cooling, the argon was evacuated and the flask backfilled with ethylene (1 atm). Toluene (75 mL) was added via syringe. The polymerization mixture was then warmed to 0°C. The solution was stirred for 30 minutes. Polymer began to precipitate from the solution within minutes. After 30 minutes, the polymerization was terminated upon exposing the catalyst to air. The polymer was precipitated from acetone, collected by filtration and washed with 6 M HCl, water, and acetone. The polymer was dried in vacuo. The polymerization yielded 1.53 g of polyethylene ( $1.3 \times 10^5$  TO).  $M_n = 91,900$ ;  $M_w = 279,000$ ;  $M_w/M_n = 3.03$ ;  $T_m = 129^\circ\text{C}$ . <sup>1</sup>H NMR (C<sub>6</sub>D<sub>5</sub>Cl, 142°C) 0.6 methyls per 100 carbons.

#### Example 142

The reaction was done in the same way as in Example 141 using 1.3 mg of  $\{[(2,6\text{-i-PrPh})_2\text{DABH}_2]\text{NiMe(Et}_2\text{O)}\}\text{BAF}^-$ .

$(i\text{-PrPh})_2\text{DABMe}_2\text{NiMe}(\text{Et}_2\text{O})\text{BAF}^+$  ( $8.3 \times 10^{-7}$  mol). The polymer was isolated as a white solid (0.1 g).

#### Examples 143-148

General procedure for the polymerization of ethylene by the methylaluminoxane (MAO) activation of nickel complexes containing bidentate diimine ligands: Polymerization at 0°C: The bisimine nickel dihalide complex ( $1.7 \times 10^{-5}$  mol) was combined with toluene (100 mL) in a flame dried Schlenk flask under 1 atmosphere ethylene pressure. The polymerization was cooled to 0°C in an ice-water bath. The mixture was stirred at 0°C for 15 minutes prior to activation with MAO. Subsequently, 1.5 mL of a 10% MAO (100 eq) solution in toluene was added onto the nickel dihalide suspension. The solution was stirred at 0°C for 10, 30, or 60 minutes. Within minutes increased viscosity and/or precipitation of polyethylene was observed. The polymerization was quenched and the polymer precipitated from acetone. The polymer was collected by suction filtration and dried under vacuum for 24 hours. See Table I for a detailed description of molecular weight and catalyst activity data.

Example No.	Catalyst
143	$[(2,6\text{-}i\text{-PrPh})_2\text{DABH}_2]\text{NiBr}_2$
144	$[(2,6\text{-}i\text{-PrPh})_2\text{DABMe}_2]\text{NiBr}_2$
145	$[(2,6\text{-MePh})_2\text{DABH}_2]\text{NiBr}_2$
146	$[(2,6\text{-}i\text{-PrPh})_2\text{DABAn}]\text{NiBr}_2$
147	$[(2,6\text{-MePh})_2\text{DABAn}]\text{NiBr}_2$
148	$[(2,6\text{-MePh})_2\text{DABMe}_2]\text{NiBr}_2$

Exam.	Condi- tions	Yield (g)	TO/ hr·mol catalyst	$M_n$	$M_w$	$M_w/M_n$	Thermal Analysis (°C)
143	0°C, 30 m	5.3	22,700	80,900	231,000	2.85	119 ( $T_m$ )
144 <sup>2</sup>	0°C, 30 m	3.8	16,300	403,000	795,000	1.97	115 ( $T_m$ )
145 <sup>3</sup>	0°C, 30 m	3.4	14,300	42,900	107,000	2.49	131 ( $T_m$ )
146 <sup>2</sup>	0°C, 30 m	7.0	29,900	168,000	389,000	2.31	107 ( $T_m$ )
147	0°C, 10 m	3.7	47,500	125,000	362,000	2.89	122 ( $T_m$ )
148	0°C, 10 m	5.1	65,400	171,000	440,000	2.58	115 ( $T_m$ )

<sup>1</sup> Polymerization reactions run at 1 atmosphere ethylene pressure.

<sup>2</sup> Branching Analysis by <sup>13</sup>C NMR per 1000 CH<sub>2</sub>:

Ex. 144: Total methyls (54.3), Methyl (43.4),

5 Ethyl (3.3), Propyl (2), Butyl (1.3), ≥Butyl and end of chains (5.7).

Ex. 146: Total methyls (90.9), Methyl (65.3),

Ethyl (7.2), Propyl (4.5), Butyl (3.5), Amyl (4.5), ≥Hexyl and end of chains (10.2).

10 <sup>3</sup> Ex. 145: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>5</sub>Cl), 142°C) 0.1 methyl per 100 carbon atoms.

#### Examples 149-154

##### Polymerization at Ambient Temperature

The general procedure described for the MAO  
15 activation of the diimine-nickel dihalides was followed in the polymerizations detailed below, except all polymerizations were run between 25-30°C.

	<u>Example No.</u>	<u>Catalyst</u>
20	149	[(2,6-i-PrPh) <sub>2</sub> DABH <sub>2</sub> ]NiBr <sub>2</sub>
	150	[(2,6-i-PrPh) <sub>2</sub> DABMe <sub>2</sub> ]NiBr <sub>2</sub>
	151	[(2,6-MePh) <sub>2</sub> DABH <sub>2</sub> ]NiBr <sub>2</sub>
	152	[(2,6-i-PrPh) <sub>2</sub> DABAn]NiBr <sub>2</sub>
	153	[(2,6-MePh) <sub>2</sub> DABAn]NiBr <sub>2</sub>
25	154	[(2,6-MePh) <sub>2</sub> DABMe <sub>2</sub> ]NiBr <sub>2</sub>

Exam.	Condi- tions <sup>1</sup>	Yield (g)	TO/ hr·mol catalyst	M <sub>n</sub>	M <sub>w</sub>	M <sub>w</sub> /M <sub>n</sub>	Thermal Analysis (°C)
149	30°C. 30 m	2.5	12,200	15,500	34,900	2.25	--
150 <sup>4</sup>	25°C. 30 m	3.4	14,500	173,000	248,000	1.44	-51 (T <sub>g</sub> )
151 <sup>3</sup>	25°C. 30 m	7.2	30,800	13,900	39,900	2.88	90,112 (T <sub>m</sub> )
152 <sup>2</sup>	25°C. 30 m	4.2	18,000	82,300	175,000	2.80	39 (T <sub>m</sub> )
153	25°C. 10 m	4.9	62,900	14,000	25,800	1.85	--
154	25°C. 10 m	3.7	47,500	20,000	36,000	1.83	--

<sup>1</sup> Polymerization reactions run at 1 atmosphere ethylene pressure.

<sup>2</sup> Branching Analysis by <sup>13</sup>C NMR per 1000 CH<sub>2</sub>:

Ex. 150: Total methyls (116.3), Methyl (93.5),  
5 Ethyl (6.2), Propyl (3.2), Butyl (2.9), Am (6.6), ≥Hex  
and end of chains (11.2).

Ex. 152: Total methyls (141.9), Methyl (98.1),  
Ethyl (15.9), Propyl (5.6), Butyl (6.8), Amyl (4.1), ≥  
Hex and end of chains (10.7). Quantitation of the -  
10 CH<sub>2</sub>CH(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>3</sub> structure per 1000 CH<sub>2</sub>'s: 8.

<sup>3</sup> Ex. 151: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>5</sub>Cl), 142°C) 3 methyl per 100  
carbon atoms.

#### Example 155

A standard solution of [(2,6-i-PrPh)<sub>2</sub>DABAN]NiBr<sub>2</sub>  
15 was prepared as follows: 1,2-difluorobenzene (10 mL)  
was added to 6.0 mg of [(2,6-i-PrPh)<sub>2</sub>DABAN]NiBr<sub>2</sub> (8.4 x  
10<sup>-6</sup> mol) in a 10 mL volumetric flask. The standard  
solution was transferred to a Kontes flask and stored  
under an argon atmosphere.

20 The standard catalyst solution (1.0 mL, 8.4 x  
10<sup>-7</sup> mol catalyst) was added to a Schlenk flask which  
contained 100 mL toluene, and was under 1 atmosphere  
ethylene pressure. The solution was cooled to 0°C, and  
1.5 mL of a 10% solution of MAO (≥1000 eq) was added.  
25 The solution was stirred for 30 minutes. Polymer began  
to precipitate within minutes. The polymerization was  
quenched and the polymer precipitated from acetone.  
The resulting polymer was dried in vacuo (2.15 g, 1.84  
x 10<sup>5</sup> TO). M<sub>n</sub> = 489,000; M<sub>w</sub> = 1,200,000; M<sub>w</sub>/M<sub>n</sub> = 2.47

30

#### Example 156

The polymerization of ethylene at 25°C was  
accomplished in an identical manner to that described  
in Example 155. The polymerization yielded 1.8 g of  
polyethylene (1.53 x 10<sup>5</sup> TO). M<sub>n</sub> = 190,000; M<sub>w</sub> =  
35 410,000; M<sub>w</sub>/M<sub>n</sub> = 2.16; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>5</sub>Cl, 142°C) 7 methyls  
per 100 carbons.

#### Example 157

A standard solution of  $[(2,6\text{-MePh})_2\text{DABAn}]\text{NiBr}_2$  was prepared in the same way as described for the complex in Example 155 using 5.0 mg of  $[(2,6\text{-MePh})_2\text{DABAn}]\text{NiBr}_2$  ( $8.4 \times 10^{-6}$  mol).

- 5 Toluene (100 mL) and 1.0 mL of the standard solution of complex 5 ( $8.3 \times 10^{-7}$  mol catalyst) were combined in a Schlenk flask under 1 atmosphere ethylene pressure. The solution was cooled to  $0^\circ\text{C}$ , and 1.5 mL of a 10% solution of MAO ( $\geq 1000$  eq) was added. The  
10 polymerization mixture was stirred for 30 minutes. The polymerization was terminated and the polymer precipitated from acetone. The reaction yielded 1.60 g of polyethylene ( $1.4 \times 10^5$  TO).  $M_n = 590,000$ ;  $M_w = 1,350,000$ ;  $M_w/M_n = 2.29$ .

15 Example 158

- Toluene (200 mL) and 1.0 mL of a standard solution of  $[(2,6\text{-i-PrPh})_2\text{DABAn}]\text{NiBr}_2$  ( $8.3 \times 10^{-7}$  mol catalyst) were combined in a Fisher-Porter pressure vessel. The resulting solution was cooled to  $0^\circ\text{C}$ , and 1.0 mL of a  
20 10% MAO ( $\geq 1000$  eq) solution in toluene was added to activate the polymerization. Subsequent to the MAO addition, the reactor was rapidly pressurized to 276 kPa. The solution was stirred for 30 minutes at  $0^\circ\text{C}$ . After 30 minutes, the reaction was quenched and polymer  
25 precipitated from acetone. The resulting polymer was dried under reduced pressure. The polymerization yielded 2.13 g of white polyethylene ( $1.82 \times 10^5$  TO).  $M_n = 611,000$ ;  $M_w = 1,400,000$ ;  $M_w/M_n = 2.29$ ;  $T_m = 123^\circ\text{C}$ ;  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_5\text{Cl}$ ,  $142^\circ\text{C}$ ) 0.5 methyls per 100 carbons.

30 Examples 159-160

Polymerization of Propylene

- The diimine nickel dihalide complex ( $1.7 \times 10^{-5}$  mol) was combined with toluene (100 mL) in a Schlenk flask under 1 atmosphere propylene pressure. The  
35 polymerization was cooled to  $0^\circ\text{C}$ , and 1.5 mL of a 10% MAO (100 eq) solution in toluene was added. The solution was stirred for 2 hours. The polymerization

was quenched and the polymer precipitated from acetone.  
The polymer was dried under vacuum.

Example No.	Catalyst
159	$[(2,6\text{-i-PrPh})_2\text{DABH}_2]\text{NiBr}_2$
160	$[(2,6\text{-i-PrPh})_2\text{DABAn}]\text{NiBr}_2$

Exam.	Condi- tions <sup>1</sup>	Yield (g)	TO/ hr-mol catalyst	M <sub>n</sub>	M <sub>w</sub>	M <sub>w</sub> /M <sub>n</sub>	Thermal Analysis (°C)
159	0°C.2h	1.3	900	131,000 a	226,000	1.72	-20 (T <sub>g</sub> )
160	0°C.2h	4.3	2,900	147,000	235,000	1.60	-78, -20 (T <sub>g</sub> )

<sup>a</sup>GPC (toluene, polystyrene standard)

Ex. 159: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>5</sub>Cl), 142°C) 30 methylys per 100 carbon atoms.

Ex. 160: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>5</sub>Cl), 142°C) 29 methylys per 100 carbon atoms. Quantitative <sup>13</sup>C NMR analysis, branching per 1000 CH<sub>2</sub>: Total methylys (699). Based on the total methylys, the fraction of 1,3-enchainment is 13%.  
Analysis of backbone carbons (per 1000 CH<sub>2</sub>): δ<sup>+</sup> (53),  
δ<sup>+</sup>/γ (0.98).

Listed below are the <sup>13</sup>C NMR data upon which the above analysis is based.

<sup>13</sup> C NMR Data	
TCB, 140C, 0.05M CrAcAc	
Freq ppm	Intensity
47.3161	53.1767
46.9816	89.3849
46.4188	82.4488
45.84	23.1784
38.4702	12.8395
38.0985	29.2643
37.472	18.6544
37.2915	24.8559
35.3747	15.6971
34.5623	14.6353
33.3145	14.2876
32.996	12.2454
30.9464	24.2132
30.6703	57.4826
30.081	30.122

γ to single branch



29.6987	29.2186	$\delta^+$ to branch
28.3659	298.691	
27.4792	33.2539	
27.1235	29.7384	
24.5324	9.45408	
21.1554	20.0541	
20.6244	110.077	
19.9926	135.356	
16.9342	8.67216	
16.4829	8.81404	
14.9962	8.38097	

Example 161

[(2,6-i-PrPh)<sub>2</sub>DABH<sub>2</sub>]NiBr<sub>2</sub> (10 mg,  $1.7 \times 10^{-5}$  mol)  
 was combined with toluene (40 mL) under a N<sub>2</sub>  
 atmosphere. A 10% solution of MAO (1.5 mL, 100 eq) was  
 5 added to the solution. After 30 minutes, the Schlenk  
 flask was backfilled with propylene. The reaction was  
 stirred at room temperature for 5.5 hours. The  
 polymerization was quenched, and the resulting polymer  
 dried under vacuum (670 mg, 213 TO/h).  $M_n = 176,000$ ;  
 10  $M_w = 299,000$ ;  $M_w/M_n = 1.70$ . Quantitative <sup>13</sup>C NMR  
 analysis, branching per 1000 CH<sub>2</sub>: Total methyls (626),  
 Methyl (501), Ethyl (1),  $\geq$ Butyl and end of chain (7).  
 Based on the total methyls, the fraction of 1,3-  
 enchainment is 22%. Analysis of backbone carbons (per  
 15 1000 CH<sub>2</sub>):  $\delta^+$  (31),  $\delta^+/\gamma$  (0.76).

Examples 162-165

The diimine nickel dihalide catalyst precursor  
 ( $1.7 \times 10^{-5}$  mol) was combined with toluene (40 mL) and 1-  
 hexene (10 mL) under a N<sub>2</sub> atmosphere. Polymerization  
 20 reactions of 1-hexene were run at both 0°C and room  
 temperature. A 10% solution of MAO (1.5 mL, 100 eq) in  
 toluene was added. Typically the polymerization  
 reactions were stirred for 1-2 hours. The polymer was  
 precipitated from acetone and collected by suction  
 25 filtration. The resulting polymer was dried under  
 vacuum.

	Ex. No.	Catalyst
	162	$[(2,6\text{-i-PrPh})_2\text{DABH}_2]\text{NiBr}_2$
	163	$[(2,6\text{-i-PrPh})_2\text{DABAn}]\text{NiBr}_2$
	164	$[(2,6\text{-i-PrPh})_2\text{DABH}_2]\text{NiBr}_2$
5	165	$[(2,6\text{-i-PrPh})_2\text{DABAn}]\text{NiBr}_2$

Exam.	Condi- tions <sup>1</sup>	Yield (g)	TO/ hr·mol catalyst	$M_n^a$	$M_w$	$M_w/M_n$	Thermal Analysis (°C)
162	25°C. 1 h	3.0	2100	173,000	318,000	1.84	-48 ( $T_g$ )
163	25°C. 1 h	1.2	860	314,000	642,000	2.05	-54 ( $T_g$ ) -19 ( $T_m$ )
164	0°C. 2 h	3.0	1100	70,800	128,000	1.80	-45 ( $T_g$ )
165	0°C. 2 h	1.5	540	91,700	142,000	1.55	-49 ( $T_g$ )

<sup>a</sup>GPC (toluene, polystyrene standards).

Branching Analysis Ex. 162: by  $^{13}\text{C}$  NMR per 1000

$\text{CH}_2$ :

10 Total methyls (157.2), Methyl (47), Ethyl (1.9),  
Propyl (4.5), Butyl (101.7),  $\geq\text{Am}$  and end of chain  
(4.3).

<sup>13</sup>C NMR data (Example 162)

TCB, 120C, 0.05M CrAcAc

<u>Freq ppm</u>	<u>Intensity</u>	
42.8364	7.99519	Methine
41.3129	27.5914	αα to two Eth <sup>+</sup> branches
40.5759	19.6201	αα to two Eth <sup>+</sup> branches
37.8831	14.7864	Methines and Methylenes
37.2984	93.6984	Methines and Methylenes
36.6684	6.99225	Methines and Methylenes
35.5773	36.067	Methines and Methylenes
34.655	55.825	Methines and Methylenes
34.3091	63.3862	Methines and Methylenes
33.8356	24.1992	Methines and Methylenes
33.428	53.7439	Methines and Methylenes
32.9957	51.1648	Methines and Methylenes
31.9169	17.4373	Methines and Methylenes
31.5546	14.008	Methines and Methylenes
31.1552	10.6667	Methines and Methylenes
30.5993	34.6931	Methines and Methylenes
30.274	56.8489	Methines and Methylenes
30.1258	42.1332	Methines and Methylenes
29.747	97.9715	Methines and Methylenes
29.1047	47.1924	Methines and Methylenes
28.8823	64.5807	Methines and Methylenes
28.1289	13.6645	Methines and Methylenes
27.5648	61.3977	Methines and Methylenes
27.1777	50.9087	Methines and Methylenes
27.0213	31.6159	Methines and Methylenes
26.9142	31.9306	Methines and Methylenes
26.4572	4.715666	Methines and Methylenes
23.2085	154.844	2B <sub>4</sub>
22.6074	12.0719	2B <sub>5</sub> <sup>+</sup> , EOC
20.0669	8.41495	1B <sub>1</sub>
19.6963	57.6935	1B <sub>1</sub>
15.9494	17.7108	
14.3477	8.98123	
13.8742	248	1B <sub>4</sub> <sup>+</sup> , EOC

Example 166

- 5 [(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>]NiBr<sub>2</sub> (10.4 mg, 1.7 x 10<sup>-5</sup> mol) was combined with toluene (15 mL) and 1-hexene (40 mL) under 1 atmosphere ethylene pressure. The solution was cooled to 0°C, and 1.5 mL of a 10% MAO (100 eq) solution in toluene was added. The reaction was
- 10 stirred at 0°C for 2.5 hours. The polymerization was quenched and the polymer precipitated from acetone. The resulting polymer was dried under reduced pressure (1.4g). Mn = 299,000; Mw = 632,000; Mw/Mn = 2.12.

Branching Analysis by  $^{13}\text{C}$  NMR per 1000  $\text{CH}_2$ : Total methyls (101.3), Methyl (36.3), Ethyl (1.3), Propyl (6.8), Butyl (47.7),  $\geq$ Amyl and end of chains (11.5).

Example 167

5         $[(2,6\text{-i-PrPh})_2\text{DABH}_2]\text{NiBr}_2$  (10 mg,  $1.7 \times 10^{-5}$  mol) was added to a solution which contained toluene (30 mL) and 1-octene (20 mL) under 1 atm ethylene. A 10% solution of MAO (1.5 mL, 100 eq) in toluene was added. The resulting purple solution was allowed to stir for 4  
10    hours at room temperature. Solution viscosity increased over the duration of the polymerization. The polymer was precipitated from acetone and dried under vacuum resulting in 5.3 g of copolymer.  $M_n = 15,200$ ,  $M_w = 29,100$ ,  $M_n/M_w = 1.92$ .

15        Example 168

$[(2,6\text{-i-PrPh})_2\text{DABAn}]\text{NiBr}_2$  (12 mg,  $1.7 \times 10^{-5}$  mol) was combined with toluene (75 mL) in a Schlenk flask under 1 atmosphere ethylene pressure. The mixture was cooled to  $0^\circ\text{C}$ , and 0.09 mL of a 1.8 M solution in toluene of  
20     $\text{Et}_2\text{AlCl}$  (10 eq) was added. The resulting purple solution was stirred for 30 minutes at  $0^\circ\text{C}$ . The polymerization was quenched and the polymer precipitated from acetone. The resulting polymer was dried under reduced pressure (6.6 g,  $2.8 \times 10^4$  TO).  $M_n$   
25    = 105,000;  $M_w = 232,000$ ;  $M_w/M_n = 2.21$

Example 169

$[(2,6\text{-i-PrPh})_2\text{DABAn}]\text{NiBr}_2$  (12 mg,  $1.7 \times 10^{-5}$  mol) was combined with toluene (75 mL) under 1 atmosphere propylene pressure. The solution was cooled to  $0^\circ\text{C}$  and  
30    0.1 mL of  $\text{Et}_2\text{AlCl}$  ( $\geq 10$  eq) was added. The reaction was stirred at  $0^\circ\text{C}$  for 2 hours. The polymerization was quenched and the polymer precipitated from acetone. The resulting polymer was dried under reduced pressure (3.97 g, 2800 TO).

35        Example 170

$[(2,6\text{-i-PrPh})_2\text{DABAn}]\text{NiBr}_2$  (12 mg,  $1.7 \times 10^{-5}$  mol) was combined with toluene (50 mL) and 1-hexene (25 mL) under a  $\text{N}_2$  atmosphere.  $\text{Et}_2\text{AlCl}$  (0.01 mL, 10 eq) was

added to the polymerization mixture. The resulting purple solution was allowed to stir for 4 hours. After 4 hours the polymerization was quenched and the polymer precipitated from acetone. The polymerization yielded  
5 1.95 g poly(1-hexene) (348 TO/h).  $M_n = 373,000$ ;  $M_w = 680,000$ ;  $M_w/M_n = 1.81$ .

#### Example 171

1-Tetradecene (20 ml) was polymerized in methylene chloride (10 ml) for 20 hr using catalyst  $\{[(2,6-i-$   
10  $\text{PrPh})_2\text{DABMe}_2\}\text{PdCH}_2\text{CH}_2\text{CH}_2\text{C(O)OCH}_3\}\text{SbF}_6^-$  (0.04 g, 0.05 mmol). The solvent and reacted monomer were removed in vacuo. The polymer was precipitated to remove unreacted monomer, by the addition of acetone to a chloroform solution. The precipitated polymer was  
15 dried in vacuo to give a 10.2 g yield.  $^{13}\text{C}$  NMR (trichlorobenzene,  $120^\circ\text{C}$ ) integrated to give the following branching analysis per 1000 methylene carbons: Total methyls (69.9), methyl (24.5), ethyl (11.4), propyl (3.7), butyl (2.3) amyl (0.3),  $\geq$ Hexyl  
20 and end of chain (24.2). Thermal analysis showed  $T_g = -42.7^\circ\text{C}$ , and  $T_m = 33.7^\circ\text{C}$  (15.2 J/g).

Listed below are the  $^{13}\text{C}$  NMR data upon which the above analysis is based.

<sup>13</sup>C NMR Data

TCB, 120C, 0.05M CrAcAc		
Freq ppm	Intensity	
39.3416	7.78511	MB <sub>2</sub>
38.2329	5.03571	MB <sub>3</sub> +
37.8616	9.01667	MB <sub>3</sub> +
37.5857	3.33517	MB <sub>3</sub> +
37.2462	31.8174	αB <sub>1</sub> , 3B <sub>3</sub>
36.6415	2.92585	αB <sub>1</sub> , 3B <sub>3</sub>
34.668	5.10337	αγ*B
34.2384	38.7927	αγ*B
33.7397	16.9614	3B <sub>5</sub>
33.3471	3.23743	3B <sub>5</sub> +, 3EOC
32.9387	16.0951	γ*γ*B, 3B <sub>4</sub>
31.9148	27.6457	γ*γ*B, 3B <sub>4</sub>
31.1297	6.03301	γ*γ*B, 3B <sub>4</sub>
30.212	59.4286	γ*γ*B, 3B <sub>4</sub>
29.7398	317.201	γ*γ*B, 3B <sub>4</sub>
29.3101	32.1392	γ*γ*B, 3B <sub>4</sub>
27.1511	46.0554	βγ*B, 2B <sub>2</sub>
27.0185	53.103	βγ*B, 2B <sub>2</sub>
26.419	9.8189	βγ*B, 2B <sub>2</sub>
24.244	2.46963	ββB
22.6207	28.924	2B <sub>5</sub> +, 2EOC
20.0479	3.22712	2B <sub>3</sub>
19.7084	18.5679	1B <sub>1</sub>
14.3929	3.44368	1B <sub>3</sub>
13.8677	30.6056	1B <sub>4</sub> +, 1EOC
10.9448	9.43801	1B <sub>2</sub>

Example 172

- 5 4-Methyl-1-pentene (20 ml) was polymerized in methylene chloride (10 ml) for 19 hr using catalyst {[(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>]PdCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C(O)OCH<sub>3</sub>}SbF<sub>6</sub><sup>-</sup> (0.04 g, 0.05 mmol). The solvent and unreacted monomer were removed in vacuo. The polymer was precipitated to
- 10 remove residual monomer by addition of excess acetone to a chloroform solution. The precipitated polymer was dried in vacuo to give a 5.7 g yield. <sup>13</sup>C NMR (trichlorobenzene, 120°C) integrated to give 518 methyls per 1000 methylene carbon atoms. Thermal
- 15 analysis showed Tg -30.3°C.

Listed below are the <sup>13</sup>C NMR data upon which the above analysis is based.

<sup>13</sup> C NMR Data	
TCB, 120C, 0.05M CrAcAc	
Freq ppm	Intensity
47.8896	13.3323
47.4011	8.54293
45.7127	26.142
45.1392	17.4909
43.9658	13.9892
43.1375	12.7089
42.6171	11.5396
41.8207	9.00437
39.203	64.9357
37.9712	24.4318
37.3075	87.438
35.4862	16.3581
34.9553	24.5286
34.35	31.8827
33.3624	25.7696
33.0226	42.2982
31.4403	25.3221
30.6226	38.7083
28.504	26.8149
27.989	81.8147
27.7341	78.3801
27.5802	94.6195
27.458	75.8356
27.0864	35.5524
25.6103	97.0113
23.4333	59.6829
23.0563	41.5712
22.536	154.144
21.9944	5.33517
20.7307	16.294
20.4971	34.7892
20.2953	29.9359
19.7378	62.0082

Example 173

1-Eicosene (19.0 g) was polymerized in methylene chloride (15 ml) for 24 hr using catalyst {[ (2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>]PdCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C(O)OCH<sub>3</sub>}SbF<sub>6</sub><sup>-</sup> (0.047 g, 0.05 mmol). The solvent and unreacted monomer were removed in vacuo. The polymer was precipitated to remove residual monomer by addition of excess acetone to a chloroform solution of the polymer. The solution was filtered to collect the polymer. The precipitated polymer was dried in vacuo to give a 5.0 g yield. <sup>13</sup>C NMR quantitative analysis, branching per 1000 CH<sub>2</sub>: Total methyls (27), Methyl (14.3), Ethyl (0), Propyl

,0.2), Butyl (0.6), Amyl (0.4),  $\geq$ Hexyl and end of chains (12.4).

Integration of the  $\text{CH}_2$  peaks due to the structure  $-\text{CH}(\text{R})\text{CH}_2\text{CH}(\text{R}')-$ , where R is an alkyl group, and R' is an alkyl group with two or more carbons showed that in 82% of these structures, R = Me.

Listed below are the  $^{13}\text{C}$  NMR data upon which the above analysis is based.

10

 $^{13}\text{C}$  NMR data

TCB, 120C, 0.05M CrAcAc

<u>Freq ppm</u>	<u>Intensity</u>	
37.7853	13.978	$\text{MB}_2^+$
37.1428	52.1332	$\alpha\text{B}$
34.1588	41.067	$\alpha\text{B}_4^+$
32.826	26.6707	$\text{MB}_1$
31.8066	24.9262	$3\text{B}_6^+, 3\text{EOC}$
30.0703	96.4154	$\gamma^+\gamma^+\text{B}, 3\text{B}_4$
29.6243	1239.8	$\gamma^+\gamma^+\text{B}, 3\text{B}_4$
27.0013	78.7094	$\text{B}\gamma^+\text{B}, (4\text{B}_5, \text{etc.})$
22.5041	23.2209	$2\text{B}_5^+, 2\text{EOC}$
19.605	30.1221	$1\text{B}_1$
13.759	23.5115	$1\text{B}_4^+, \text{EOC}$

Example 174

The complex  $[(2,6\text{-i-PrPh})_2\text{DABH}_2]\text{PdMeCl}$  (0.010 g, 0.019 mmol) and norbornene (0.882 g, 9.37 mmol) were weighed into a vial and dissolved in 2 ml  $\text{CH}_2\text{Cl}_2$ . NaBAF (0.032g, 0.036 mmol) was rinsed into the stirring mixture with 2 ml of  $\text{CH}_2\text{Cl}_2$ . After stirring about 5 minutes, there was sudden formation of a solid precipitate. Four ml of o-dichlorobenzene was added and the solution became homogenous and slightly viscous. After stirring for 3 days, the homogeneous orange solution was moderately viscous. The polymer was precipitated by addition of the solution to excess MeOH, isolated by filtration, and dried in vacuo to give 0.285 g (160 equivalents norbornene per Pd) bright orange glassy solid. DSC (two heats,  $15^\circ\text{C}/\text{min}$ ) showed no thermal events from  $-50$  to  $300^\circ\text{C}$ . This is consistent with addition type poly(norbornene). Ring-opening polymerization of norbornene is known to



produce an amorphous polymer with a glass transition temperature of about 30-55°C.

Example 175

The solid complex  $\{[(2,6-i-$   
5  $\text{PrPh})_2\text{DABH}_2]\text{PdMe}(\text{Et}_2\text{O})\}\text{SbF}_6^-$  (0.080 g, 0.10 mmol) was added as a solid to a stirring solution of norbornene (1.865 g) in 20 ml of o-dichlorobenzene in the drybox. About 30 min after the start of the reaction, there was slight viscosity (foam on shaking) and the homogeneous  
10 mixture was dark orange/red. After stirring for 20 h, the solvent and unreacted norbornene were removed in vacuo to give 0.508 g orange-red glassy solid (54 equivalents norbornene/Pd).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): broad featureless peaks from 0.8-2.4 ppm, no peaks in the  
15 olefinic region. This spectrum is consistent with addition type poly(norbornene). GPC (trichlorobenzene, 135°C, polystyrene reference, results calculated as linear polyethylene using universal calibration theory):  $\text{Mn}=566$   $\text{Mw}=1640$   $\text{Mw/Mn}=2.90$ .

20 Example 176

4-Methyl-1-pentene (10 ml) and ethylene (1 atm) were copolymerized in 30 ml of chloroform according to example 125 using catalyst  $\{[(2,6-i-$   
25  $\text{PrPh})_2\text{DABMe}_2]\text{PdCH}_2\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OCH}_3\}\text{SbF}_6^-$  (0.084 g, 0.10 mmol) to give 23.29 g highly viscous yellow oil. The  $^1\text{H}$  NMR spectrum was similar to the poly(ethylene) of example 110 with 117 methyl carbons per 1000 methylene carbons.  $^{13}\text{C}$  NMR quantitative analysis, branching per 1000  $\text{CH}_2$ : Total methyls (117.1), Methyl (41.5), Ethyl  
30 (22.7), Propyl (3.3), Butyl (13), Amyl (1.2),  $\geq$ Hexyl and end of chains (33.1),  $\geq$ Amyl and end of chains (42.3), By  $^{13}\text{C}$  NMR this sample contains two identifiable branches at low levels attributable to 4-methyl-1-pentene. The Bu and  $\geq$ Amyl peaks contain small  
35 contributions from isopropyl ended branch structures.

Example 177

$\text{CoCl}_2$  (500 mg, 3.85 mmol) and  $(2,6-i-\text{PrPh})_2\text{DABAn}$  (2.0 g, 4.0 mmol) were combined as solids and dissolved

in 50 mL of THF. The brown solution was stirred for 4 hours at 25°C. The solvent was removed under reduced pressure resulting in a brown solid (1.97 g, 82% yield).

- 5 A portion of the brown solid (12 mg) was immediately transferred to another Schlenk flask and dissolved in 50 mL of toluene under 1 atmosphere of ethylene. The solution was cooled to 0°C, and 1.5 mL of a 10% MAO solution in toluene was added. The  
10 resulting purple solution was warmed to 25°C and stirred for 12 hours. The polymerization was quenched and the polymer precipitated from acetone. The white polymer (200 mg) was collected by filtration and dried under reduced pressure.  $M_n = 225,000$ ,  $M_w = 519,000$ ,  
15  $M_w/M_n = 2.31$ ,  $T_g = -42^\circ$ ,  $T_m = 52^\circ\text{C}$  and  $99.7^\circ\text{C}$ .

Example 178

- Ethyl 10-undecenoate (10 ml) and ethylene (1 atm) were copolymerized in 30 ml of  $\text{CH}_2\text{Cl}_2$  according to example 125 using catalyst  $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdCH}_2\text{CH}_2\text{CH}_2\text{C(O)OCH}_3\}\text{SbF}_6^-$  (0.084 g, 0.10 mmol). The copolymer was precipitated by removing most of the  $\text{CH}_2\text{Cl}_2$  in vacuo, followed by addition of excess acetone. The solution was decanted and the copolymer was dried in vacuo to give 1.35 g viscous fluid.  $^1\text{H}$   
20 NMR ( $\text{CDCl}_3$ ): 0.75-0.95(m,  $\text{CH}_3$ ); 0.95-1.5(m, -C(O)OCH<sub>2</sub>CH<sub>3</sub>,  $\text{CH}_2$ , CH); 1.5-1.7(m, -CH<sub>2</sub>CH<sub>2</sub>C(O)OCH<sub>2</sub>CH<sub>3</sub>); 1.9-2.0(m, -CH<sub>2</sub>CH=CH-); 2.3(t, -CH<sub>2</sub>CH<sub>2</sub>C(O)OCH<sub>2</sub>CH<sub>3</sub>); 4.15(q, -CH<sub>2</sub>CH<sub>2</sub>C(O)OCH<sub>2</sub>CH<sub>3</sub>); 5.40(m, -CH=CH-). The olefinic and allylic peaks are due to isomerized ethyl  
30 10-undecenoate which has coprecipitated with the copolymer. Adjusting for this, the actual weight of copolymer in this sample is 1.18 g. The copolymer was reprecipitated by addition of excess acetone to a chloroform solution.  $^1\text{H}$  NMR of the reprecipitated  
35 polymer is similar except there are no peaks due to isomerized ethyl 10-undecenoate at 1.9-2.0 and 5.40 ppm. Based on integration, the reprecipitated copolymer contains 7.4 mole % ethyl 10-undecenoate, and

53 methyl carbons per 1000 methylene carbons.  $^{13}\text{C}$  NMR quantitative analysis, branching per 1000  $\text{CH}_2$ : Total methyls (84.5), Methyl (31.7), Ethyl (16.9), Propyl (1.5), Butyl (7.8), Amyl (4.4),  $\geq$ Hexyl and end of chains (22.3). GPC (THF, PMMA standard):  $M_n=20,300$   $M_w=26,300$   $M_w/M_n = 1.30$ .  $^{13}\text{C}$  NMR quantitative analysis, branching per 1000  $\text{CH}_2$ : ethyl ester (37.8), Ester branches  $-\text{CH}(\text{CH}_2)_n\text{CO}_2\text{CH}_2\text{CH}_3$  as a % of total ester:  $n \geq 5$  (65.8),  $n=4$  (6.5),  $n=1,2,3$  (26.5),  $n=0$  (1.2).

Listed below are the  $^{13}\text{C}$  NMR data upon which the above analysis is based.

<sup>13</sup>C NMR Data

Freq ppm	Intensity
59.5337	53.217
39.7234	2.57361
39.3145	7.80953
38.2207	11.9395
37.8437	20.3066
37.2225	29.7808
36.7181	5.22075
34.6792	17.6322
34.265	107.55
33.7181	21.9369
33.3093	8.22574
32.9164	15.0995
32.396	8.52655
32.0828	5.79098
31.9075	37.468
31.127	13.8003
30.6757	8.38026
30.2084	52.5908
29.9961	27.3761
29.72	151.164
29.5076	39.2815
29.2899	69.7714
28.727	6.50082
27.5164	20.4174
26.9908	64.4298
26.5713	9.18236
26.3749	11.8136
25.5519	4.52152
25.0528	43.7554
24.2457	7.9589
23.1094	10.0537
22.9926	4.71618
22.6156	37.2966
20.0245	2.4263
19.6847	25.9312
19.1643	5.33693
17.5183	2.20778
14.2954	66.1759
13.8653	43.8215
13.414	2.52882
11.1521	5.9183
10.9237	14.9294
174.945	3.27848
172.184	125.486
171.695	4.57235

Example 179

The solid complex  $\{[(2,6\text{-i-PrPh})_2\text{DABH}_2]\text{PdMe}(\text{Et}_2\text{O})\}\text{SbF}_6^-$  (0.080 g, 0.10 mmol) was  
 5 added as a solid to a stirring solution of cyclopentene  
 (1.35 g, 20 mmol) in 20 ml of dichlorobenzene in the

drybox. After stirring 20 h, the slightly viscous solution was worked up by removing the solvent in vacuo to give 1.05 g sticky solid (156 equivalents of cyclopentene per Pd).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): complex spectrum from 0.6-2.6 ppm with maxima at 0.75, 1.05, 1.20, 1.55, 1.65, 1.85, 2.10, 2.25, and 2.50. There is also a multiplet for internal olefin at 5.25-5.35. This is consistent with a trisubstituted cyclopentenyl end group with a single proton (W. M. Kelly et. al., Macromolecules 1994, 27, 4477-4485.) Integration assuming one olefinic proton per polymer chain gives  $\text{DP}=8.0$  and  $\text{Mn}=540$ . IR (Thin film between NaCl plates,  $\text{cm}^{-1}$ ): 3048 (vw, olefinic end group, CH stretch), 1646 (vw, olefinic end group,  $\text{R}_2\text{C}=\text{CHR}$  trisubstituted double bond stretch), 1464 (vs), 1447 (vs), 1364 (m), 1332 (m), 1257 (w), 1035 (w), 946 (m), 895 (w), 882 (w), 803 (m, cyclopentenyl end group,  $\text{R}_2\text{C}=\text{CHR}$  trisubstituted double bond, CH bend), 721 (vw, cyclopentenyl end group,  $\text{RHC}=\text{CHR}$  disubstituted double bond, CH bend). GPC (trichlorobenzene,  $135^\circ\text{C}$ , polystyrene reference, results calculated as linear polyethylene using universal calibration theory):  $\text{Mn}=138$   $\text{Mw}=246$   $\text{Mw}/\text{Mn}=1.79$ .

#### Example 180

The solid complex  $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdCH}_2\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OCH}_3\}\text{SbF}_6^-$  (0.084 g, 0.10 mmol) was added to a stirring solution of 10.0 ml cyclopentene in 10 ml  $\text{CHCl}_3$  in the drybox. After stirring for 20 h, the mixture appeared to be separated into two phases. The solvent and unreacted monomer were removed in vacuo leaving 2.20 g off-white solid (323 equivalents cyclopentene per Pd). DSC (25 to  $300^\circ\text{C}$ ,  $15^\circ\text{C}/\text{min}$ , first heat):  $\text{Tg} = 107^\circ\text{C}$ ,  $\text{Tm}$  (onset) =  $165^\circ\text{C}$ ,  $\text{Tm}$  (end) =  $260^\circ\text{C}$ , Heat of fusion =  $29 \text{ J/g}$ . Similar results were obtained on the second heat. GPC (trichlorobenzene,  $135^\circ\text{C}$ , polystyrene reference, results calculated as linear polyethylene using

universal calibration theory):  $M_n=28,700$   $M_w=33,300$   
 $M_w/M_n=1.16$ .

Listed below are the  $^{13}\text{C}$  NMR analysis for this polymer.

5

$^{13}\text{C}$ NMR Data	
TCB, 120°C, 0.05M CrAcAc	
Freq ppm	Intensity
46.4873	142.424
38.339	59.7617
30.5886	137.551

#### Example 181

The solid complex  $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdCH}_2\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OCH}_3\}\text{SbF}_6^-$  (0.084 g, 0.10 mmol) was added to a stirring solution of 10.0 ml cyclopentene in 10 ml  $\text{CHCl}_3$  in a Schlenk flask. The flask was evacuated briefly and refilled with ethylene. It was maintained under slightly above 1 atm ethylene pressure using a mercury bubbler. After 20 h, the solvent and unreacted monomers were removed in vacuo from the homogeneous solution to give 12.89 g of highly viscous fluid.  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ): cyclopentene peaks: 0.65(m, 1H); 1.15(broad s, 2H); 1.5-2.0(m, 5H); ethylene peaks: 0.75-0.95(m,  $\text{CH}_3$ ); 0.95-1.5(m, CH and  $\text{CH}_2$ ). Integration shows 24 mole % cyclopentene in this copolymer. Analysis of the polyethylene part of the spectrum (omitting peaks due to cyclopentyl units) shows 75 total methyl carbons per 1000 methylene carbons. Based on quantitative  $^{13}\text{C}$  analysis, the distribution of branches per 1000 methylene carbons is Methyl (21), Ethyl (13), Propyl (-0), Butyl (20) and  $\geq$  Amyl (20). DSC (first heat: 25 to 150°C, 10°C/min; first cool: 150 to -150°C, 10°C/min; second heat: -150 to 150°C, 10°C/min; values of second heat reported):  $T_g = -33^\circ\text{C}$ ,  $T_m = 19^\circ\text{C}$  (11 J/g). GPC (trichlorobenzene, 135°C, polystyrene reference, results calculated as linear polyethylene using universal calibration theory):  $M_n=3,960$   $M_w=10,800$   $M_w/M_n=2.73$ .

Listed below are the  $^{13}\text{C}$  NMR data upon which the above analysis is based.

 $^{13}\text{C}$  NMR Data

TCB, 120C, 0.05M CrAcAc

Freq ppm	Intensity	
48.344	1.85262	
46.5562	22.8938	1 cme and/or 1,3 ccmcc
44.9064	10.8003	1,3 cme
42.0842	16.824	
40.7845	117.364	2 eme
40.5777	113.702	1,3 eme
40.3336	136.742	1,3 eme
39.5591	15.0962	methylene from 2 cmc or/and 2 cme
38.7634	18.636	
38.4716	12.3847	
38.2488	17.3939	
37.2144	17.5837	
36.721	111.057	
36.2913	11.0136	
35.8776	22.0367	
35.6176	90.3685	
34.5248	15.734	
34.1959	24.7661	
33.0182	14.0261	
31.8671	238.301	
31.4056	20.6401	
30.8433	11.2412	
30.4613	20.2901	
30.0104	62.2997	
29.7133	78.3272	
29.2359	31.6111	
28.9653	53.5526	
28.6577	64.0528	
26.9813	17.6335	
26.3925	4.51208	
25.9363	5.6969	
24.2971	1.70709	
22.9019	9.13305	2B <sub>4</sub>
22.6048	14.3641	2B <sub>5</sub> +, 2EOC
19.7349	10.124	1B <sub>1</sub>
19.1991	2.00384	1B <sub>1</sub>
17.5811	2.28331	end group
13.8783	26.3448	1B <sub>4</sub> +, 1EOC
12.6264	19.6468	end group
10.9501	4.96188	1B <sub>2</sub>

Example 182

1-Pentene (10 ml) and cyclopentene (10 ml) were copolymerized in 20 ml of o-dichlorobenzene solvent according to example 180. After 72 h, the unreacted monomers and part of the solvent were removed in vacuo to give 3.75 g highly viscous fluid. Analysis by  $^1\text{H}$  NMR showed that this material contained 1.81 g of copolymer; the remainder was o-dichlorobenzene. The  $^1\text{H}$  NMR spectrum was very similar to poly(ethylene-co-cyclopentene) in Example 181. Integration shows 35 mole % cyclopentene in this copolymer. Analysis of the poly(1-pentene) part of the spectrum (omitting peaks due to cyclopentyl units) shows 62 methyl carbons per 1000 methylene carbons. The fraction of  $\omega,1$ -enchainment (chain straightening) in this section is 72%. Based on quantitative  $^{13}\text{C}$  analysis, the distribution of branches per 1000 methylene carbons is Methyl (36), Propyl (7), and  $\geq$ Amyl (20). DSC (first heat: -150 to 150  $^{\circ}\text{C}$ , 15  $^{\circ}\text{C}/\text{min}$ ; first cool: 150 to -150  $^{\circ}\text{C}$ , 15  $^{\circ}\text{C}/\text{min}$ ; second heat: -150 to 150  $^{\circ}\text{C}$ , 15  $^{\circ}\text{C}/\text{min}$ ; values of second heat reported):  $T_g = -19^{\circ}\text{C}$ ,  $T_m = 50^{\circ}\text{C}$  (24 J/g). GPC (trichlorobenzene, 135 $^{\circ}\text{C}$ , polystyrene reference, results calculated as linear polyethylene using universal calibration theory):  $M_n=14,900$   $M_w=27,300$   $M_w/M_n=1.82$

Example 183

A 100 mL autoclave was charged with chloroform (40 mL), methyl acrylate (10 mL),  $\{[(2,6\text{-EtPh})_2\text{DABMe}_2]\text{PdMe}(\text{NCMe})\}\text{BAF}^-$  (0.100 g, 0.073 mmol), and ethylene (2.1 MPa). The reaction mixture was stirred under 1.4 MPa of ethylene for 180 min; during this time the temperature inside the reactor remained between 25 and 26 $^{\circ}\text{C}$ . The ethylene pressure was then vented, and the crude reaction mixture discharged from the reactor. The reactor was washed with 2 x 50 mL of chloroform. The washings were added to the crude reaction mixture; 250 mL of methanol was added to the resulting solution. After standing overnight, the polymer product had

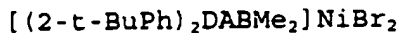


recipitated from solution; it was isolated by decanting off the chloroform/methanol solution, and dried giving 3.91 g of an extremely viscous oil.  $^1\text{H}$  NMR of this material showed it to be ethylene/methyl acrylate copolymer, containing 1.1 mole% methyl acrylate. The polymer contained 128 methyl-ended hydrocarbon branches per 1000 methylenes, and 7 methyl ester ended branches per 1000 methylenes.

Example 184

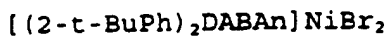
10 A solution of  $\{[(\text{Np})_2\text{DABMe}_2]\text{PdMe}(\text{NCMe})\}\text{SbF}_6^-$  (0.027 g, 0.02 mmol) in 5 mL  $\text{CDCl}_3$  was agitated under 1.4 MPa of ethylene for 3 h; during this time the temperature inside the reactor varied between 25 and 40°C.  $^1\text{H}$  NMR of the solution indicated the presence of ethylene  
15 oligomers.  $M_n$  was calculated on the basis of  $^1\text{H}$  NMR integration of aliphatic vs. olefinic resonances to be 100. The degree of polymerization, DP, was calculated on the basis of the  $^1\text{H}$  NMR spectrum to be 3.8; for a linear polymer this would result in 500 methyl-ended  
20 branches per 1000 methylenes. However, based on the  $^1\text{H}$  NMR spectrum the number of methyl-ended branches per 1000 methylenes was calculated to be 787.

Example 185



25 A Schlenk tube was charged with 0.288 g (0.826 mmol) of  $(2\text{-t-BuPh})_2\text{DABMe}_2$ , which was then dissolved in 15 mL of  $\text{CH}_2\text{Cl}_2$ . This solution was cannulated onto a suspension of  $(\text{DME})\text{NiBr}_2$  (0.251 g, 0.813 mmol) in 15 mL of  $\text{CH}_2\text{Cl}_2$ . The reaction mixture was allowed to stir  
30 overnight, resulting in a deep red solution. The solution was filtered and the solvent evaporated under vacuum. The remaining orange, oily residue was washed with ether (2 x 10 mL) and dried under vacuum to give an orange/rust powder (0.36 g, 78%).

35 Example 186



$(2\text{-t-BuPh})_2\text{DABAn}$  (0.202 g, 0.454 mmol) and  $(\text{DME})\text{NiBr}_2$  (0.135 g, 0.437 mmol) were combined and

stirred in 25 mL of CH<sub>2</sub>Cl<sub>2</sub>, as in Example 185. An orange/rust solid was isolated (0.18g, 62%).

Example 187

[(2,5-t-BuPh)<sub>2</sub>DABAn]NiBr<sub>2</sub>

- 5 The corresponding diimine (0.559 g, 1.00 mmol) and (DME)NiBr<sub>2</sub> (0.310 g, 1.00 mmol) were combined and stirred in 35 mL of CH<sub>2</sub>Cl<sub>2</sub>, as was done in Example 185. An orange solid was isolated (0.64 g, 83%).

Examples 188-190

- 10 Polymerizations were carried out at 0°C and under 1 atmosphere of ethylene pressure. The (diimine)NiBr<sub>2</sub> complex (1.4-1.7 x 10<sup>-5</sup> mol) was placed into a flame-dried Schlenk flask and dissolved in 100 mL of toluene. The flask was placed under ethylene and cooled in an  
15 ice bath. Polymerization was initiated by addition of 100 equivalents (1.5 mL 10% soln in toluene) of methylaluminoxane (MAO). The reaction mixture was stirred for 30 or 120 minutes at constant temperature followed by quenching with 6M HCl. Polymer was  
20 precipitated from the resulting viscous solution with acetone, collected via filtration, and dried under vacuum for 24 h. A summary of results is shown below.

	Ex No.	Catalyst
	188	[(2-t-BuPh) <sub>2</sub> DABMe <sub>2</sub> ]NiBr <sub>2</sub>
25	189	[(2-t-BuPh) <sub>2</sub> DABAn]NiBr <sub>2</sub>
	190	[(2,5-t-BuPh) <sub>2</sub> DABAn]NiBr <sub>2</sub>

Exam.	Catalyst (10 <sup>-5</sup> mol)	Conditions	Yield (g)	TO/hr·mol catalyst
188	(1.7)	0°C. 120 m	9.88	10,500
189	(1.4)	0°C. 30 m	8.13	40,500
190	(1.5)	0°C. 30 m	6.60	31,000

Examples 191-196

- 30 General Procedure. The procedure of Example 84 for the homopolymerization of ethylene) was followed with the exception that the acrylate was added to the

reaction mixture at  $-78^{\circ}\text{C}$  immediately following the addition of 50 mL of  $\text{CH}_2\text{Cl}_2$ . Polymerizations are at room temperature (rt) and 1 atm ethylene unless stated otherwise. The copolymers were generally purified by filtering an  $\text{Et}_2\text{O}$  or petroleum ether solution of the polymer through Celite and/or neutral alumina.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopic data and GPC analysis are consistent with the formation of random copolymers. In addition to the polyethylene resonances, the following resonances diagnostic of acrylate incorporation were observed:

Methyl Acrylate:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  3.64 (s, OMe), 2.28 (t,  $J = 7.48$ ,  $\text{OCH}_2$ ), 1.58 (m,  $\text{OCH}_2\text{CH}_2$ );  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 100 MHz)  $\delta$  176 (C(O)), 50.9 (C(O)OMe).

Fluorinated Octyl Acrylate (FOA, 3M Co. Minneapolis, MN):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  4.58 (t,  $J = 13.51$ ,  $\text{OCH}_2(\text{CF}_2)_6\text{CF}_3$ ), 2.40 (t,  $J = 7.32$ ,  $\text{C(O)CH}_2$ ), 1.64 (m,  $\text{C(O)CH}_2\text{CH}_2$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  172.1 (C(O)), 59.3 (t,  $J_{\text{CF}} = 27.0$ ,  $\text{OCH}_2(\text{CF}_2)_6\text{CF}_3$ ).

Ex.	Catalyst (R), conc. ( $10^{-3}$ Molar)	Acrylate, conc. (Molar)	Run Time (h)	Yield (g)	% Acrylate Inc. molt/wt%	# CH <sub>3</sub> /1000 CH <sub>2</sub>	$M_w$	$M_n$	PDI
191	Me, 2.3	o Me, 6.7	24 <sup>a</sup>	≈0.5	10.9/ 27.3	134			
192	Me, 1.4	o Me, 1.1	48	3.94	2.7/ 7.84	114	77000	56400	1.4 b
193	Me, 2.0	FOA, .74	24	27.5	0.80/ 11.58	110			
194	Me, 2.0	FOA, 1.3	24	20.7	0.80/ 11.58	126			
195	H, 2.0	FOA, .74	24	1.49	0.31/ 4.85	144			
196	2.0 <sup>c</sup>	FOA, .74	24	2.00	0.71/ 10.73	135			

<sup>a</sup>Final 3 h at  $50^{\circ}\text{C}$ .

<sup>b</sup>THF, PMMA standards.

<sup>c</sup>Catalyst is  $\{[(2,6-i-$

$\text{PrPh})\text{DABAn}\}\text{PdCH}_2\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OCH}_2(\text{CF}_2)_6\text{CF}_3\}\text{BAF}^-$

### Examples 197-203

In Examples 197-203, structures of the type  
5 represented by (VI) and (IX) are described.

### Example 197

$\{[(2,6-i-\text{PrPh})_2\text{DABMe}_2]\text{PdMe}(\text{H}_2\text{C}=\text{CH}_2)\}\text{BAF}^-$  and

$\{[(2,6-i-\text{PrPh})_2\text{DABMe}_2]\text{Pd}(\text{P})\text{H}_2\text{C}=\text{CH}_2)\}\text{BAF}^-$

In a drybox under an argon atmosphere, an NMR tube  
10 was charged with -0.01 mmol of  $\{[(2,6-i-\text{PrPh})_2\text{DABMe}_2]\text{PdMe}\}_2(\mu-\text{Cl})\text{BAF}^-/[(\text{Na}(\text{OEt})_2)_2\text{BAF}$  or  $\text{NaBAF}]$   
or  $\{[(2,6-i-\text{PrPh})_2\text{DABMe}_2]\text{PdMe}(\text{OEt}_2)\}\text{BAF}^-$ . The tube was  
then capped with a septum, removed from the drybox, and  
cooled to  $-78^\circ\text{C}$ . Via gastight syringe, 700  $\mu\text{L}$  of  
15  $\text{CD}_2\text{Cl}_2$  was then added to the NMR tube and the septum  
was wrapped with Parafilm. The tube was shaken very  
briefly in order to dissolve the palladium complex.  
After acquiring a spectrum at  $-80^\circ\text{C}$ , 1 - 10 equiv of  
olefin was added to the  $-78^\circ\text{C}$  solution via gastight  
20 syringe, and the olefin was dissolved in the solution  
by briefly shaking the NMR tube. The tube was then  
transferred to the cold NMR probe and spectra were  
acquired. This olefin complex was prepared from both  
precursors using one equiv of ethylene:  $^1\text{H}$  NMR  
25 ( $\text{CD}_2\text{Cl}_2$ , 400 MHz,  $-60^\circ\text{C}$ )  $\delta$  7.72 (s, 8, BAF:  $\text{C}_\text{O}$ ), 7.54  
(s, 4, BAF:  $\text{C}_\text{P}$ ), 7.4 - 7.0 (m, 6,  $\text{H}_{\text{aryl}}$ ), 4.40 (s, 4,  
 $\text{H}_2\text{C}=\text{CH}_2$ ), 3.38 (br m, 4,  $\text{O}(\text{CH}_2\text{CH}_3)_2$ ), 2.69 (septet, 2,  $\text{J}$   
= 6.73,  $\text{CHMe}_2$ ), 2.63 (septet, 2,  $\text{J}$  = 6.80,  $\text{C}'\text{HMe}_2$ ),  
2.34 and 2.23 (s, 3 each,  $\text{N}=\text{C}(\text{Me})-\text{C}'(\text{Me})=\text{N}$ ), 1.33 (d,  
30 6,  $\text{J}$  = 6.80,  $\text{C}'\text{HMeMe}'$ ), 1.25 (d, 6,  $\text{J}$  = 6.50,  $\text{CHMeMe}'$ ),  
1.14 (d, 6,  $\text{J}$  = 7.00,  $\text{CHMeMe}'$ ), 1.10 (br m, 6,  
 $\text{O}(\text{CH}_2\text{CH}_3)_2$ ), 1.07 (d, 6,  $\text{J}$  = 6.80,  $\text{C}'\text{HMeMe}'$ ), 0.18  
( $\text{PdMe}$ );  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 100 MHz,  $-60^\circ\text{C}$ )  $\delta$  180.3 and  
174.7 ( $\text{N}=\text{C}-\text{C}'=\text{N}$ ), 161.5 (q,  $\text{J}_{\text{BC}}$  = 49.6, BAF:  $\text{C}_{\text{ipso}}$ ),  
35 143.3 and 141.7 (Ar, Ar':  $\text{C}_{\text{ipso}}$ ), 134.4 (BAF:  $\text{C}_\text{O}$ ), 128.6  
(Ar:  $\text{C}_\text{P}$ ), 128.4 (q,  $\text{J}_{\text{BC}}$  = 32.3, BAF:  $\text{C}_\text{M}$ ), 127.7 (Ar':  
 $\text{C}_\text{P}$ ), 124.7 and 124.4 (Ar, Ar':  $\text{C}_\text{O}$ ), 117.3 (BAF:  $\text{C}_\text{P}$ ),  
91.7 ( $\text{J}_{\text{CH}}$  = 160.7,  $\text{H}_2\text{C}=\text{CH}_2$ ), 65.8 ( $\text{O}(\text{CH}_2\text{CH}_3)_2$ ), 28.9

(CHMe<sub>2</sub>), 28.8 (C'HMe<sub>2</sub>), 24.1, 23.4, 22.9 and 22.7 (CHMeMe', C'HMeMe'), 21.7 and 21.5 (N=C(Me)=C'(Me)=N), 15.0 (OCH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>, 4.3 (PdMe).

In the presence of 5 equiv of ethylene, chain growth was observed at -35°C. Spectral data for {[(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>]Pd(P)(CH<sub>2</sub>=CH<sub>2</sub>)}BAF<sup>-</sup> [wherein P is as defined for (VI)] intermediates (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz, -35°C) are reported in the following table:

{[(2,6-i-PrPh) <sub>2</sub> DABMe <sub>2</sub> ]Pd[(CH <sub>2</sub> ) <sub>n</sub> CH <sub>3</sub> ](H <sub>2</sub> C=CH <sub>2</sub> )} <sup>+</sup> BAF <sup>-</sup>									
n	H <sub>2</sub> C=CH <sub>2</sub>		N=C(Me)-C'(Me)=N				Pd(CH <sub>2</sub> ) <sub>n</sub> Me		
	mult.	δ	mult.	δ	mult.	δ	mult.	J	δ
0	s	4.42	s	2.35	s	2.24	s		0.22
2	s	4.36	s	2.37	s	2.22	t	7.00	0.39
4	s	4.36	s	2.37	s	2.22	t	7.20	0.62

10

Addition of 15 more equiv of ethylene and warming to room temperature leads to complete consumption of ethylene and the observance of a single organometallic species: <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz, 24.0°C) δ 7.74 (s, 8, BAF: C<sub>O</sub>), 7.19 (s, 4, BAF: H<sub>P</sub>), 2.85 (br m, 4, CHMe<sub>2</sub>, C'HMe<sub>2</sub>), 2.36 and 2.23 (s, 3 each, N=C(Me)-C'(Me)=N), 1.5 - 1.0 (CHMeMe', C'HMeMe'), 1.29 (Pd(CH<sub>2</sub>)<sub>n</sub>CH<sub>3</sub>), 0.89 (Pd(CH<sub>2</sub>)<sub>n</sub>CH<sub>3</sub>).

15

#### Example 198

20 {[(2,6-i-PrPh)<sub>2</sub>DABH<sub>2</sub>]PdMe(H<sub>2</sub>C=CH<sub>2</sub>)}BAF<sup>-</sup> and {[(2,6-i-PrPh)<sub>2</sub>DABH<sub>2</sub>]Pd(P)(H<sub>2</sub>C=CH<sub>2</sub>)}BAF<sup>-</sup>

This olefin complex, {[(2,6-i-PrPh)<sub>2</sub>DABH<sub>2</sub>]PdMe(H<sub>2</sub>C=CH<sub>2</sub>)}BAF<sup>-</sup>, was prepared following the procedure of example 197 by both of the analogous synthetic routes used in example 197, using one equiv of ethylene: <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz, -60°C) δ 8.42 and 8.26 (s, 1 each, N=C(H)-C'(H)=N), 7.72 (s, 8, BAF: H<sub>O</sub>), 7.54 (s, 4, BAF: H<sub>P</sub>), 7.42 - 7.29 (m, 6, H<sub>aryl</sub>), 4.60 (s, H<sub>2</sub>C=CH<sub>2</sub>), 3.37 (q, 4, J = 7.03, (O(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 2.89 (septet, 2, J = 6.71, CHMe<sub>2</sub>), 2.76 (septet, 2, J = 6.68, C'HMe<sub>2</sub>), 1.35 (d, 6, J = 6.72, C'HMeMe'), 1.29

30

- (d, 6,  $J = 6.79$ , CHMeMe'), 1.15 (d, 6,  $J = 6.72$ , CHMeMe'), 1.09 (d, 6,  $J = 6.54$ , C'HMeMe'), 1.15 (t, 6,  $J = 7.34$ , O(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 0.46 (s, 3, PdMe); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz, -60°C)  $\delta$  167.7 ( $J_{CH} = 182$ , N=C(H)), 162.8 ( $J_{CH} = 182$ , N=C'(H)), 161.4 (q,  $J = 49.8$ , BAF: C<sub>ipso</sub>), 140.2 and 139.8 (Ar, Ar': C<sub>ipso</sub>), 138.6 and 137.3 (Ar, Ar': C<sub>O</sub>), 134.4 (BAF: C<sub>O</sub>), 129.2 and 129.1 (Ar, Ar': C<sub>p</sub>), 128.3 (q,  $J_{CF} = 32.2$ , BAF: C<sub>m</sub>), 124.3 and 124.0 (Ar, Ar': C<sub>m</sub>), 124.2 (q,  $J_{CF} = 272.5$ ; BAF: CF<sub>3</sub>), 117.3 (BAF: C<sub>p</sub>), 92.7 ( $J_{CH} = 162.5$ , H<sub>2</sub>C=CH<sub>2</sub>), 65.8 (O(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 28.9 and 28.7 (CHMe<sub>2</sub> and C'HMe<sub>2</sub>), 25.1, 24.0, 22.0 and 21.9 (CHMeMe', C'HMeMe'), 15.12 ( $J_{CH} = 139.2$ , PdMe), 15.09 (O(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>).

- In the presence of 10 equiv of ethylene, chain growth was monitored at -35°C. Diagnostic <sup>1</sup>H NMR spectral data (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz, -35°C) for the second title compound are reported in the following table:

$\{[(2.6\text{-}i\text{-PrPh})_2\text{DABH}_2]\text{Pd}[(\text{CH}_2)_n\text{CH}_3](\text{H}_2\text{C}=\text{CH}_2)\}^+\text{BAF}^-$									
n	N=C(H)-C'(H)=N				H <sub>2</sub> C=CH <sub>2</sub>		Pd(CH <sub>2</sub> ) <sub>n</sub> Me		
	mult.	$\delta$	mult.	$\delta$	mult.	$\delta$	mult.	J	$\delta$
0 <sup>a</sup>	s	8.42	s	8.27	br s	4.6	s		0.50
2 <sup>b</sup>	s	8.41	s	8.24	br s	4.6	t	7.85	0.36
4	s	8.41	s	8.24	br s	4.6	t	7.15	0.62
6	s	8.41	s	8.24	br s	4.6	t	7.25	0.76
>6	s	8.41	s	8.24	br s <sup>c</sup>	4.6	m		0.85 <sup>d</sup>

- <sup>a</sup>For  $n = 0$ :  $\delta$  2.91 and 2.71 (septet, 2 each, CHMe<sub>2</sub>, C'HMe<sub>2</sub>), 1.38, 1.32, 1.18 and 1.12 (d, 6 each, CHMeMe', C'HMeMe'). <sup>b</sup>For  $n > 0$ :  $\delta$  2.91 and 2.71 (septet, 2 each, CHMe<sub>2</sub>, C'HMe<sub>2</sub>), 1.37, 1.35, 1.16 and 1.11 (d, 6 each, CHMeMe', C'HMeMe'). <sup>c</sup>In the absence of free ethylene, bound ethylene appears as a sharp singlet at 4.56 ppm. <sup>d</sup> $\delta$  1.27 (Pd(CH<sub>2</sub>)<sub>n</sub>CH<sub>3</sub>).

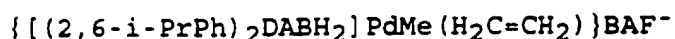
After the ethylene was consumed at -35°C, the sample was cooled to -95°C. Broad upfield multiplets were observed at -7.2 to -7.5 ppm and - 8.0 to -8.5 ppm. The sample was then warmed to room temperature

and a spectrum was acquired. No olefins were detected, the upfield multiplets were no longer observable, and a single organometallic species was present:  $^1\text{H}$  NMR

( $\text{CD}_2\text{Cl}_2$ , 400 MHz,  $19.8^\circ\text{C}$ )  $\delta$  8.41 and 8.28 (s, 1 each,  $\text{N}=\text{C}(\text{H})-\text{C}'(\text{H})=\text{N}$ ), 7.72 (s, 8, BAF:  $\text{H}_\text{O}$ ), 7.56 (s, 4, BAF:  $\text{H}_\text{P}$ ), 3.09 (m, 4,  $\text{CHMe}_2$ ,  $\text{C}'\text{HMe}_2$ ), 1.35, 1.32, 1.26 and 1.22 (d, 6 each,  $\text{J} = 6.5-6.8$ ,  $\text{CHMeMe}'$ ,  $\text{C}'\text{HMeMe}'$ ), 1.27 ( $\text{Pd}(\text{CH}_2)_n\text{CH}_3$ ), 0.88 ( $\text{Pd}(\text{CH}_2)_n\text{CH}_3$ ).

A second spectrum was acquired 12 minutes later at room temperature. Substantial decomposition of the organometallic species was observed.

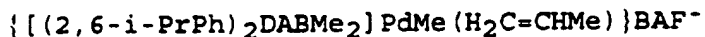
#### Example 199



This olefin complex,  $\{[(2,6\text{-MePh})_2\text{DABH}_2]\text{PdMe}(\text{H}_2\text{C}=\text{CH}_2)\}\text{BAF}^-$ , was prepared following the procedure in example 197, using  $\{[(2,6\text{-MePh})_2\text{DABH}_2]\text{PdMe}(\text{OEt}_2)\}\text{BAF}^-$  and one equiv of ethylene:  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 300 MHz,  $-70^\circ\text{C}$ )  $\delta$  8.46 and 8.31 (s, 1 each,  $\text{N}=\text{C}(\text{H})-\text{C}'(\text{H})=\text{N}$ ), 7.72 (s, 8, BAF:  $\text{H}_\text{O}$ ), 7.52 (s, 4, BAF:  $\text{H}_\text{P}$ ), 7.4 - 6.4 (m, 6,  $\text{H}_{\text{aryl}}$ ), 4.56 (s, 4,  $\text{H}_2\text{C}=\text{CH}_2$ ), 2.19 and 2.16 (s, 6 each, Ar, Ar': Me), 0.31 (s, 3, PdMe).

In the presence of 10 equiv of ethylene (eq 3), olefin insertion was monitored at  $-30^\circ\text{C}$  and the production of cis- and trans-2-butenes was observed.

#### Example 200



This olefin complex,  $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdMe}(\text{H}_2\text{C}=\text{CHMe})\}\text{BAF}$ , was prepared following the procedure of Example 197, using  $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdMe}(\text{OEt}_2)\}\text{BAF}^-$  and one equiv of propylene:  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 400 MHz,  $-61^\circ\text{C}$ )  $\delta$  7.73 (s, 8, BAF:  $\text{H}_\text{O}$ ), 7.55 (s, 4, BAF:  $\text{H}_\text{P}$ ), 7.4 - 7.0 (m, 6,  $\text{H}_{\text{aryl}}$ ), 5.00 (m, 1  $\text{H}_2\text{C}=\text{CHMe}$ ), 4.24 (d, 1,  $\text{J} = 9.1$ ,  $\text{HH}'\text{C}=\text{CHMe}$ ), 4.23 (d, 1,  $\text{J} = 14.8$ ,  $\text{HH}'\text{C}=\text{CHMe}$ ), 3.38 (br q, 4,  $\text{J} = 6.50$ ,  $\text{O}(\text{CH}_2\text{CH}_3)_2$ ), 2.84 (septet, 1,  $\text{J} = 6.5$ , Ar:  $\text{CHMe}_2$ ), 2.68 (m, 3, Ar:  $\text{C}'\text{HMe}_2$ ; Ar':  $\text{CHMe}_2$ ,  $\text{C}'\text{HMe}_2$ ), 2.32 and 2.22 (s, 3 each,  $\text{N}=\text{C}(\text{Me})-\text{C}'(\text{Me})=\text{N}$ ), 1.63 (d, 3,  $\text{J} = 6.40$ ,

$\text{H}_2\text{C}=\text{CHMe}$ ), 1.35, 1.30, 1.25, 1.1, 1.1, 1.04 (d, 3 each,  $J = 6.4 - 6.7$ , Ar: C'HMeMe'; Ar': CHMeMe', C'HMeMe'), 1.24 and 1.1 (d, 3 each,  $J = 6.4$ , Ar: CHMeMe'), 1.1 (m, 6,  $\text{O}(\text{CH}_2\text{CH}_3)_2$ ), 0.28 (PdMe);  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 100 MHz,  $-61^\circ\text{C}$ )  $\delta$  179.9 and 174.7 ( $\text{N}=\text{C}-\text{C}'=\text{N}$ ), 161.5 (q,  $J_{\text{BC}} = 49.7$ , BAF: Cipso), 138.8, 137.9, 137.8, 137.7, 137.0 and 136.9 (Ar: Cipso,  $\text{C}_\text{O}$ ,  $\text{C}_\text{O}'$ ; Ar': Cipso,  $\text{C}_\text{O}$ ,  $\text{C}_\text{O}'$ ); 134.4 (BAF:  $\text{C}_\text{O}$ ), 128.6 and 128.5 (Ar:  $\text{C}_\text{P}$ ,  $\text{C}_\text{P}'$ ), 128.4 (q,  $J_{\text{CF}} = 31.6$ , BAF:  $\text{C}_\text{m}$ ), 124.8, 124.7, 124.4 and 124.4 (Ar:  $\text{C}_\text{m}$ ,  $\text{C}_\text{m}'$ ; Ar':  $\text{C}_\text{m}$ ,  $\text{C}_\text{m}'$ ), 124.2 (q,  $J_{\text{CF}} = 272.5$ , BAF:  $\text{CF}_3$ ), 117.3 (BAF:  $\text{C}_\text{P}$ ), 116.1 ( $J_{\text{CH}} = 155.8$ ,  $\text{H}_2\text{C}=\text{CHMe}$ ), 85.6 ( $J_{\text{CH}} = 161.4$ ,  $\text{H}_2\text{C}=\text{CHMe}$ ), 65.8 ( $\text{O}(\text{CH}_2\text{CH}_3)_2$ ), 28.9, 28.7, 28.7, 28.7 (Ar:  $\text{CHMe}_2$ , C'HMe<sub>2</sub>; Ar':  $\text{CHMe}_2$ , C'HMe<sub>2</sub>), 24.5, 23.9, 23.5, 23.4, 22.9, 22.9, 22.8, 22.2, 21.71, 21.65, 20.9 ( $\text{H}_2\text{C}=\text{CHMe}$ ; Ar: CHMeMe', C'HMeMe'; Ar': CHMeMe', C'HMeMe',  $\text{N}=\text{C}(\text{Me})-\text{C}'(\text{Me})=\text{N}$ ), 16.9 ( $J_{\text{CH}} = 137.5$ , PdMe), 15.0 ( $\text{O}(\text{CH}_2\text{CH}_3)_2$ ).

#### Example 201

$\{[(2,6\text{-i-PrPh})_2\text{DABH}_2]\text{PdMe}(\text{H}_2\text{C}=\text{CHMe})\}\text{BAF}^-$  and  $\{[(2,6\text{-i-PrPh})_2\text{DABH}_2]\text{Pd}(\text{P})(\text{H}_2\text{C}=\text{CHMe})\}\text{BAF}^-$   
 This olefin complex,  $\{[(2,6\text{-i-PrPh})_2\text{DABH}_2]\text{PdMe}(\text{H}_2\text{C}=\text{CHMe})\}\text{BAF}^-$ , was prepared following using both of the synthetic routes used in Example 197, using one equiv of propylene:  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 400 MHz,  $-80^\circ\text{C}$ )  $\delta$  8.40 and 8.24 (s, 1 each,  $\text{N}=\text{C}(\text{H})-\text{C}'(\text{H})=\text{N}$ ), 7.72 (s, 8, BAF:  $\text{H}_\text{O}$ ), 7.53 (s, 4, BAF:  $\text{H}_\text{P}$ ), 7.40 - 7.27 (m, 6, Haryl), 5.41 (br m,  $\text{H}_2\text{C}=\text{CHMe}$ ), 4.39 (d, 1,  $J = 8.09$ ,  $\text{HH}'\text{C}=\text{CHMe}$ ), 4.14 (br d, 1,  $J = 15.29$ ,  $\text{HH}'\text{C}=\text{CHMe}$ ), 3.10 (br m, 1,  $\text{CHMe}_2$ ), 2.87 (overlapping septets, 2, C'HMe<sub>2</sub>, C''HMe<sub>2</sub>), 2.59 (br septet, 1, C'''HMe<sub>2</sub>), 1.64 (d,  $J = 6.07$ ,  $\text{H}_2\text{C}=\text{CHMe}$ ), 1.39 and 1.03 (d, 3 each,  $J = 6.4$ , CHMeMe'), 1.27, 1.27, 1.14 and 1.1 (d, 3 each,  $J = 5.9 - 6.7$ , C'HMeMe', C''HMeMe'), 1.23 and 1.1 (d, 3 each,  $J = 6.8$ , C'''HMeMe'), 0.47 (PdMe);  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 100 MHz,  $-80^\circ\text{C}$ )  $\delta$  167.1 ( $J_{\text{CH}} = 181.6$ ,  $\text{N}=\text{C}(\text{H})$ ), 163.0 ( $J_{\text{CH}} = 182.1$ ,  $\text{N}=\text{C}'(\text{H})$ ), 161.3 (q,  $J_{\text{BC}} = 50.0$ , BAF: Cipso), 140.5 and 140.0 (Ar, Ar': Cipso), 138.5, 138.3, 137.7 and 137.2 (Ar:  $\text{C}_\text{O}$ ,  $\text{C}_\text{O}'$ ; Ar':  $\text{C}_\text{O}$ ,  $\text{C}_\text{O}'$ ),



- 134.2 (BAF: C<sub>O</sub>), 128.9 and 128.8 (Ar, Ar': C<sub>p</sub>), 128.1 (q, J<sub>CF</sub> = 31.1, BAF: C<sub>m</sub>), 124.0 (q, J<sub>CF</sub> = 272.5, BAF: CF<sub>3</sub>), 124.6, 123.8, 123.8 and 123.6 (Ar: C<sub>m</sub>, C<sub>m</sub>'; Ar': C<sub>m</sub>, C<sub>m</sub>'), 117.1 (BAF: C<sub>p</sub>), 116.4 (J<sub>CH</sub> = 160.3, H<sub>2</sub>C=CHMe), 85.4 (J<sub>CH</sub> = 159.9, H<sub>2</sub>C=CHMe), 65.7 (O(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 29.2, 28.7, 28.5 and 28.0 (Ar: CHMe<sub>2</sub>, C'HMe<sub>2</sub>; Ar': CHMe<sub>2</sub>, C'HMe<sub>2</sub>), 26.0, 24.4, 24.03, 23.97, 23.7, 21.9, 21.8, 21.7 and 21.6 (H<sub>2</sub>C=CHMe; Ar: CHMeMe', C'HMeMe'; Ar': CHMeMe', C'HMeMe'), 16.6 (J<sub>CH</sub> = 142.1, PdMe), 15.0 (O(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>).

In the presence of 10 equiv of propylene, chain growth was monitored at -20°C, thus enabling {[(2,6-i-PrPh)<sub>2</sub>DABH<sub>2</sub>]Pd[(CHMeCH<sub>2</sub>)Me](H<sub>2</sub>C=CHMe)}<sup>+</sup>BAF<sup>-</sup>, intermediates to be observed (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz, -20°C):

15

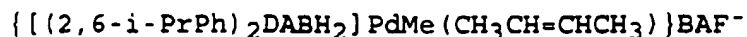
$\{[(2,6-i-PrPh)_2DABMe_2]Pd((CHMeCH_2)_nMe)(H_2C=CHMe)\}^+BAF^-$													
n	N=CHC'H=N		HH'C=CHMe			HH'C=CHMe			C=CHMe		(CHMeCH <sub>2</sub> ) <sub>n</sub> Me		
	δ	δ	mult	J	δ	mult	J	δ	mult	δ	mult	J	δ
0	8.40	8.26	d	14.4	4.25	d	8.6	4.47	m	5.45	s		0.59
1	8.38	8.24	d	14.4	3.98	d	7.4	4.25	m	5.55	t	7.1	0.51
>1	8.39	8.23	d	13.7	4.07	d	8.0	4.41	m	5.42			

### Example 202

- The compound {[(2,6-i-PrPh)<sub>2</sub>DABH<sub>2</sub>]PdMe(H<sub>2</sub>C=CHCH<sub>2</sub>Me)}<sup>+</sup>BAF<sup>-</sup> was made using both the synthetic methods described in Example 197, except 1-butene was used. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz, -75°C) δ 8.44 and 8.28 (s, 1 each, N=C(H)-C'(H)=N), 7.74 (s, 8, BAF: C<sub>O</sub>), 7.56 (s, 4, BAF: C<sub>p</sub>), 7.5 - 7.2 (m, 6, H<sub>aryl</sub>), 5.4 (m, 1, H<sub>2</sub>C=CHCH<sub>2</sub>CH<sub>3</sub>), 4.36 (d, 1, J = 8.2, HH'C=CHCH<sub>2</sub>CH<sub>3</sub>), 4.13 (br m, 1, HH'C=CHCH<sub>2</sub>CH<sub>3</sub>), 3.14, 2.92, 2.92 and 2.62 (m, 1 each, Ar, Ar': CHMe<sub>2</sub>, C'HMe<sub>2</sub>), 1.95 and 1.65 (m, 1 each, H<sub>2</sub>C=CHCHH'CH<sub>3</sub>), 1.5 - 1.0 (d, 3 each, Ar, Ar': CHMeMe', C'HMeMe'), 0.60 (s, 3, PdMe).
- Isomerization to cis- and trans-2-butene began at -78°C and was monitored at -15°C along with chain

growth. For Pd[P] species, formation of the 1-butene complex occurred selectively in the presence of *cis*- and *trans*-2-butene. Consumption of all olefins was observed at 20°C.

5

Examples 203

Experiments involving the reaction of the bispalladium( $\mu$ -Cl) compound/NaBAF (as in Example 197) with *trans*-2-butene and the bispalladium( $\mu$ -Cl) compound alone with *cis*-2-butene led to partial formation of the corresponding olefin complexes. An equilibrium was observed between the ether adduct and the olefin adduct when a compound of the type  $\{[(2,6\text{-}i\text{-PrPh})_2\text{DABH}_2]\text{PdMe}(\text{OEt}_2)\}\text{BAF}^-$  was reacted with one equiv of *cis*- or *trans*-2-butene. Addition of excess 2-butene led to complete formation of the olefin adduct. Chain growth, which was monitored at 0°C to room temperature, led to complete consumption of butenes. Some butene isomerization occurred during the course of the oligomerization and small amounts of  $\beta$ -hydride elimination products (disubstituted internal olefins and trisubstituted olefins) were observed. Oligomer methylene and methyl groups were observed at 1.3 and 0.8 ppm, respectively. Diagnostic  $^1\text{H}$  NMR spectral data for the butene complexes follows:

$\{[(2,6\text{-}i\text{-PrPh})_2\text{DABH}_2]\text{PdMe}(\text{trans-CH}_3\text{CH}=\text{CHCH}_3)\}\text{BAF}^-$ .  
 $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 400 MHz, -39°C)  $\delta$  8.43 and 8.29 (s, 1 each,  $\text{N}=\text{C}(\text{H})-\text{C}(\text{H})=\text{N}$ ), 5.27 and 4.72 (m, 1 each,  $\text{CH}_3\text{CH}=\text{C}'\text{HCH}_3$ ), 0.73 (PdMe);  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 100 MHz, -95°C)  $\delta$  166.8 ( $\text{J}_{\text{CH}} = 181.5$ ,  $\text{N}=\text{C}(\text{H})$ ), 163.2 ( $\text{J}_{\text{CH}} = 179.8$ ,  $\text{N}=\text{C}'(\text{H})$ ), 161.2 (q,  $\text{J}_{\text{BC}} = 49.5$ , BAF:  $\text{C}_{\text{ipso}}$ ), 141.3 and 139.9 (Ar, Ar':  $\text{C}_{\text{ipso}}$ ), 138.4, 138.2, 138.0 and 137.0 (Ar, Ar':  $\text{C}_o$ ,  $\text{C}_o'$ ), 134.0 (BAF:  $\text{C}_o$ ), 128.74 and 128.71 (Ar, Ar':  $\text{C}_p$ ), 128.0 (q,  $\text{J}_{\text{CF}} = 31.9$ , BAF:  $\text{C}_m$ ), 125.4 ( $\text{J}_{\text{CH}} = 150.0$ , free  $\text{MeCH}=\text{CHMe}$ ), 123.8 (q,  $\text{J}_{\text{CF}} = 272.5$ , BAF:  $\text{CF}_3$ ), 124.8, 123.7, 123.5 and 123.4 (Ar, Ar':  $\text{C}_o$ ,  $\text{C}_o'$ ), 117.0 (BAF:  $\text{C}_p$ ), 107.0 and 106.8 ( $\text{J}_{\text{CH}}=152$ ,  $\text{MeCH}=\text{C}'\text{HMe}$ ), 65.6 (free  $\text{O}(\text{CH}_2\text{CH}_3)_2$ ), 29.5, 28.3, 27.6,

35

26.5, 24.1, 23.8, 23.6, 21.5, 21.3, 21.2, 20.4, 19.9, 19.6, 17.9, 17.5 (Ar, Ar': CHMeMe', C'HMeMe'; MeCH=C'HMe), 17.7 (free MeCH=CHMe), 15.0 (PdMe), 14.7 (O(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>).

- 5 {[(2,6-i-PrPh)<sub>2</sub>DABH<sub>2</sub>]PdMe(cis-CH<sub>3</sub>CH=CHCH<sub>3</sub>)}BAF'. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz, -75°C) δ 8.37 and 8.25 (s, 1 each, N=C(H)-C'(H)=N), 5.18 (q, 2, CH<sub>3</sub>CH=CHCH<sub>3</sub>), 1.63 (d, 6, J = 4.9, CH<sub>3</sub>CH=CHCH<sub>3</sub>), 0.47 (PdMe).

- References for the synthesis of bis(oxazoline) ligands and their transition metal complexes: Corey, 10 E. J.; Imai, N.; Zang, H. Y. J. Am. Chem. Soc. 1991, 113, 728-729. Pfaltz, A. Acc. Chem. Res. 1993, 26, 339-345, and references within.

#### Example 204

- 15 2,2-bis{2-[4(S)-methyl-1,3-oxazolinyl]}propane (500 mg, 2.38 mmol) was dissolved in 10 mL CH<sub>2</sub>Cl<sub>2</sub> in a Schlenk tube under a N<sub>2</sub> atmosphere. This solution was added via cannula to a suspension of (1,2-dimethoxyethane)NiBr<sub>2</sub> (647 mg, 2.10 mmol) in 30 mL of 20 CH<sub>2</sub>Cl<sub>2</sub>. The solution was stirred for 18 hours. The solvent was evaporated under reduced pressure. The product, 2,2-bis{2-[4(S)-methyl-1,3-oxazolinyl]}propaneNi(Br<sub>2</sub>), was washed with 3 x 15 mL of hexane. The product was isolated as a purple powder 25 (0.85 g, 84% yield).

#### Example 205

- The product of Example 204 (14.2 mg, 3.3 x 10<sup>-5</sup> mol) and toluene (75 mL) were combined in a Schlenk flask under 1 atmosphere ethylene pressure. The 30 solution was cooled to 0°C, and 3.0 mL of a 10% MAO (100 eq) solution in toluene was added. The resulting yellow solution was stirred for 40 hours. The oligomerization was quenched by the addition of H<sub>2</sub>O and a small amount of 6 M HCl. The organic fraction was 35 separated from the aqueous fraction, and the toluene was removed under reduced pressure. A colorless oil resulted (0.95 g of oligomer). This illustrates that polymerization may be effected by such Pd, Ni and/or Co

isoxazoline complexes which are substituted in both 4 positions of the oxazoline ring by hydrocarbyl and substituted hydrocarbyl groups.

Example 206

5

$[(\text{COD})\text{PdMe}(\text{NCMe})]^+\text{BAF}^-$

To  $\text{CODPdMeCl}$  (100mg, 0.37 mmol) was added a solution of acetonitrile (0.08 mL, 1.6 mmol) in 25 mL  $\text{CH}_2\text{Cl}_2$ . To this colorless solution was added  $\text{Na}^+\text{BAF}^-$  (370 mg, 0.4 mmol). A white solid immediately  
10 precipitated. The mixture was stirred at  $-20^\circ\text{C}$  for 2 hours. The solution was concentrated and filtered. Removal of solvent under reduced pressure resulted in a glassy solid.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  5.78 (mult, 2H),  $\delta$  5.42 (mult, 2H),  $\delta$  2.65 (mult, 4H),  $\delta$  2.51 (9mult, 4H),  $\delta$   
15 2.37 (s, 3H, NCMe),  $\delta$  1.19 (s, 3H, Pd-Me),  $\delta$  7.72 (s, 8,  $\text{BAF}^-$ ,  $\text{H}_\text{O}$ ),  $\delta$  7.56 (s, 4,  $\text{BAF}^-$ ,  $\text{H}_\text{P}$ ).

Example 207

$[(2,6-(i\text{-Pr})_2\text{PhDABH}_2)\text{NiBr}_2]$  (10 mg,  $1.7 \times 10^{-5}$  mol), toluene (13 mL), and 1-hexene (38 mL) were combined in  
20 a Schlenk flask under an argon atmosphere. A 10% MAO solution (1.5 mL, 100 eq) in toluene was added to a suspension of the diimine nickel dihalide. The resulting purple solution was stirred at room temperature for 1 hour. The polymerization was  
25 quenched and the polymer precipitated from acetone. The resulting colorless polymer was dried in vacuo (2.5 g). GPC (toluene, polystyrene standards)  $M_n = 330,000$ ;  $M_w = 590,000$ ;  $M_n/M_w = 1.8$ .

Example 208

$[(2,6-i\text{-PrPh})_2\text{DABH}_2]\text{NiBr}_2$  (10 mg,  $1.7 \times 10^{-5}$  mol) was added to a solution which contained toluene (30 mL) and 1-octene (20 mL). A 10% solution of MAO (1.5 mL, 100 eq) in toluene was added. The resulting purple  
30 solution was allowed to stir for 4 hours at room temperature. Solution viscosity increased over the duration of the polymerization. The polymer was precipitated from acetone and dried in vacuo resulting

in 5.3 g of copolymer.  $M_n = 15,200$ ;  $M_w = 29,100$ ;  $M_w/M_n = 1.92$ .

#### Example 209

5  $[(2,6\text{-}i\text{-PrPh})_2\text{DABMe}_2]\text{Ni}(\text{CH}_3)_2$  (20 mg,  $4.1 \times 10^{-5}$  mol) and MAO (35.7 mg, 15eq) were combined as solids in an NMR tube. The solid mixture was cooled to  $-78^\circ\text{C}$  and dissolved in 700  $\mu\text{L}$  of  $\text{CD}_2\text{Cl}_2$ . While cold, 10  $\mu\text{L}$  of ether  $\text{d}^{10}$  was added to stabilize the incipient cation.  $^1\text{H}$  NMR spectrum were recorded at 253, 273, and  $293^\circ\text{K}$ .  
10 It was apparent that the starting nickel dimethyl complex was disappearing and a new nickel complex(es) was being formed. Activation of the dimethyl complex was occurring through methane loss ( $s, \delta$  0.22). After 2 hours at  $293^\circ\text{K}$  all of the starting species had  
15 disappeared. To test for ethylene polymerization activity, 5000  $\mu\text{L}$  (10eq) of ethylene was added via gas tight syringe to the solution at  $-78^\circ\text{C}$ . The consumption of ethylene was monitored by  $^1\text{H}$  NMR spectroscopy. The onset of ethylene uptake was  
20 observed at  $223^\circ\text{K}$  and all of the ethylene was consumed upon warming the probe to  $293^\circ\text{K}$ . The persistence of the Ni-Me signal during the experiment suggests that under these conditions propagation is faster than initiation. Solid polyethylene was observed upon  
25 removing the NMR tube from the probe.

#### Example 210

$[(2,6\text{-}i\text{-PrPh})_2\text{DABAn}]\text{NiBr}_2$  (12 mg,  $1.7 \times 10^{-5}$  mol) was combined with toluene (50 mL) and 1-hexene (25 mL) under a  $\text{N}_2$  atmosphere.  $\text{Et}_2\text{AlCl}$  (0.01 mL, 10 eq) was  
30 added to the polymerization mixture. The resulting purple solution was allowed to stir for 4 hours. After 4 hours the polymerization was quenched and the polymer precipitated from acetone. The polymerization yielded 2.05 g poly(1-hexene) (731 TO). (GPC, toluene,  
35 polystyrene standards)  $M_n = 305,000$ ;  $M_w = 629,000$ ;  $M_w/M_n = 2.05$ .  $T_g = -57^\circ\text{C}$ ,  $T_m = 52^\circ\text{C}$ .  $T_m = -57^\circ\text{C}$ ,  $T_g = -20^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_5\text{Cl}$ ,  $142^\circ\text{C}$ ) 10 methyls per 100

carbons. This number is significantly less than would be expected for strictly atactic 1-hexene.

Example 211

Concentration dependence on catalyst activity in  
5 nickel catalyzed polymerization of  $\alpha$ -olefins. A series  
of homopolymerizations of 1-hexene were run at 10%,  
15%, 20%, 30%, 40%, and 75% 1-hexene by volume. In  
each of the above cases 10 mg of [(2,6-i-  
PrPh)<sub>2</sub>DABH<sub>2</sub>]NiBr<sub>2</sub> was taken up in toluene and 1-hexene  
10 (50 mL total volume 1-hexene + toluene). All of the  
polymerizations were run at 25°C and activated by the  
addition of 1.5 mL of a 10% MAO solution in toluene.  
The polymerizations were stirred for 1 hour and  
quenched upon the addition of acetone. The polymer was  
15 precipitated from acetone and dried in vacuo. 10% by  
volume 1-hexene yielded 2.5 g poly(1-hexene), 15% by  
volume 1-hexene yielded 2.6 g poly(1-hexene), 20% by  
volume 1-hexene yielded 3.0 g poly(1-hexene), 30% by  
volume 1-hexene yielded 2.6 g poly(1-hexene), 40% by  
20 volume 1-hexene yielded 2.6 g poly(1-hexene), 75% by  
volume 1-hexene yielded 2.5 g poly(1-hexene).

Example 212

FeCl<sub>2</sub> (200 mg, 1.6 mmol) and 20 ml of CH<sub>2</sub>Cl<sub>2</sub> were  
combined in a Schlenk flask under an argon atmosphere.  
25 In a separate flask, 550 mg (2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub> and 20  
ml CH<sub>2</sub>Cl<sub>2</sub> were combined, resulting in a yellow  
solution. The ligand solution was slowly (2 hr)  
transferred via cannula into the suspension of FeCl<sub>2</sub>.  
The resulting solution was stirred at 25°C. After 4  
30 hr. the solution was separated from the unreacted FeCl<sub>2</sub>  
by filter cannula (some purple solid was also left  
behind). The solvent was removed in vacuo to give a  
purple solid (0.53 g, 71% yield). A portion of the  
purple solid was combined with 50 ml of toluene under 1  
35 atm of ethylene. The solution was cooled to 0°C, and 6  
ml of a 10% MAO solution in toluene was added. The  
mixture was warmed to 25°C and stirred for 18 hr. The  
polymer was precipitated by acetone, collected by

suction filtration, and washed with 6M HCl, water and acetone. The white polymer was dried under reduced pressure. Yield 13 mg.

Example 213

- 5           A 58-mg (0.039-mmol) sample of  $\{[(2,6-i-PrPh)_2DABMe_2]PdCH_2CH_2CH_2C(O)OCH_3\} BAF^-$  was placed in a 600-mL stirred autoclave under nitrogen with 150mL of deaerated water. This mixture was pressurized to 5.5 MPa with ethylene and was stirred at 23°C for 68 hr.
- 10   When the ethylene was vented, the autoclave was found to be full of rubbery polymer: on top was a layer of white, fluffy elastomeric polyethylene, while beneath was gray, dense elastomeric polyethylene. The water was poured out of the autoclave; it was a hazy light
- 15   blue, containing a tiny amount of emulsified polyethylene; evaporation of the whole aqueous sample yielded a few mg of material. The product was dried under high vacuum to yield 85.5g of amorphous elastomeric polyethylene, which exhibited a glass
- 20   transition temperature of -61°C and a melting endotherm of -31°C (16J/g) by differential scanning calorimetry. H-1 NMR analysis ( $CDCl_3$ ): 105 methyl carbons per 1000 methylene carbons. Gel permeation chromatography (trichlorobenzene, 135°C, polystyrene reference,
- 25   results calculated as polyethylene using universal calibration theory):  $M_n=42,500$ ;  $M_w=529,000$ ;  $M_w/M_n=12.4$ . This example demonstrates the use of pure water as a polymerization medium.

Example 214

- 30           A 73-mg (0.049 mmol) sample of  $\{[(2,6-i-PrPh)_2DABMe_2]PdCH_2CH_2CH_2C(O)OCH_3\} BAF^-$  was placed in a 600-mL stirred autoclave under nitrogen with 150mL of deaerated water; to this was added 3.1 mL (3.3g) of Triton<sup>®</sup> X-100 nonionic surfactant. This mixture was
- 35   pressurized to 5.8 MPa with ethylene and was stirred at 23°C for 17 hr. When the ethylene was vented, most of the emulsion came out the valve due to foaming; it was caught in a flask. There was polymer suspended in the

emulsion; this was filtered to give, after MeOH and acetone washing and air-drying, 2.9g of amorphous polyethylene as a fine, gray rubber powder. The filtrate from the suspended polymer was a clear gray solution; this was concentrated on a hot plate to yield recovered Triton® X-100 and palladium black. There was no polymer in the aqueous phase. The elastomeric polyethylene product exhibited a glass transition temperature of -50°C and a melting endotherm of 48°C (5J/g) by differential scanning calorimetry. H-1 NMR analysis (CDCl<sub>3</sub>): 90 methyl carbons per 1000 methylene carbons. Gel permeation chromatography (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal calibration theory):  $M_n=31,000$ ;  $M_w=311,000$ ;  $M_w/M_n=10.0$ . This example demonstrates the aqueous emulsion polymerization of ethylene in the presence of a non-ionic surfactant.

#### Example 215

A 93-mg (0.110-mmol) sample of  $\{[(2,6-i-PrPh)_2DABMe_2]PdCH_2CH_2CH_2C(O)OCH_3\}^+SbF_6^-$  was placed in a 600-mL stirred autoclave under nitrogen with 150mL of deaerated water; to this was added 0.75g (1.4 mmol) of FC-95® anionic fluorosurfactant (potassium perfluorooctansulfonate). This mixture was pressurized to 5.1 MPa with ethylene and was stirred at 23°C for 15 hr. The ethylene was vented; the product consisted of polymer suspended in emulsion as well as some polymer granules on the wall of the autoclave; the emulsion was filtered to give, after MeOH and acetone washing and air-drying, 2.4g of amorphous polyethylene as a fine, gray rubber powder. The hazy blue-gray aqueous filtrate was evaporated to yield 0.76g of residue; hot water washing removed the surfactant to leave 0.43g of dark brown sticky polyethylene rubber. H-1 NMR (CDCl<sub>3</sub>) analysis: 98 CH<sub>3</sub>'s per 1000 CH<sub>2</sub>'s. Differential scanning calorimetry: melting point: 117°C (111J/g); glass transition: -31°C (second heat; no apparent Tg on



first heat). This example demonstrates the aqueous emulsion polymerization of ethylene in the presence of an anionic surfactant. This example also demonstrates that a true aqueous emulsion of polyethylene can be  
5 obtained by emulsion polymerization of ethylene with these catalysts in the presence of an appropriate surfactant.

#### Example 216

A 90-mg (0.106-mmol) sample of  $\{[(2,6-i-PrPh)_2DABMe_2]PdCH_2CH_2CH_2C(O)OCH_3\}^+SbF_6^-$  was placed in a  
10 600-mL stirred autoclave under nitrogen with 150mL of deaerated water; to this was added 0.75g (2.1 mmol) of cetyltrimethylammonium bromide cationic surfactant. This mixture was pressurized to 5.2 MPa with ethylene  
15 and was stirred for 66 hr at 23°C. The ethylene was vented; the product consisted of polymer suspended in a dark solution; this was filtered to give, after MeOH and acetone washing and air-drying, 0.13g of amorphous polyethylene as a tacky, gray rubber powder. There was  
20 no polymer in the aqueous phase. H-1 NMR ( $CDCl_3$ ) analysis: 96  $CH_3$ 's per 1000  $CH_2$ 's. Differential scanning calorimetry: glass transition: -58°C; melting endotherms: 40°, 86°, 120°C (total: 20J/g). This example demonstrates the aqueous emulsion  
25 polymerization of ethylene in the presence of a cationic surfactant.

#### Example 217

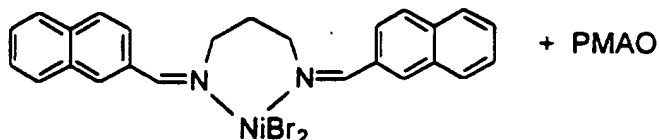
An 87-mg (0.103-mmol) sample of  $\{[(2,6-i-PrPh)_2DABMe_2]PdCH_2CH_2CH_2C(O)OCH_3\}^+SbF_6^-$  was placed in a  
30 600-mL stirred autoclave under nitrogen. To this was added 100 mL of dry, deaerated methyl acrylate containing 100 ppm of phenothiazine as a free-radical polymerization inhibitor. The autoclave was stirred and pressurized to 300 psig with ethylene over 5 min.  
35 The autoclave was then pressurized to 600 psig with an additional 300 psig of carbon monoxide (300 psig  $E + 300$  psig  $CO = 600$  psig). The reaction was stirred for 20 hr at 23°C as the autoclave pressure dropped to 270

psig. The ethylene was then vented; the autoclave contained a yellow solution which was concentrated by rotary evaporation, taken up in methylene chloride, filtered, and again concentrated to yield 0.18g of dark brown viscous oil. The product was washed with hot acetone to remove the brown catalyst residues and was held under high vacuum to yield 55 mg of a colorless, viscous liquid terpolymer. The infrared spectrum exhibited carbonyl absorbances at 1743 (ester), 1712 (ketone), and 1691  $\text{cm}^{-1}$ . H-1 NMR ( $\text{CDCl}_3$ ) analysis: 76  $\text{CH}_3$ 's per 1000  $\text{CH}_2$ ; there were peaks at 2.3 (t,  $\text{CH}_2\text{COOR}$ ), 2.7 (m,  $\text{CH}_2\text{CO}$ ), and 3.66 ppm ( $\text{COOCH}_3$ ). The polymer contained 3.3 mol% MA (9.4 wt% MA). The carbon monoxide content was not quantified, but the absorbance in the infrared spectrum of the polymer due to ketone was about 1/2 to 2/3 the absorbance due to acrylate ester. This example demonstrates the use of carbon monoxide as a monomer.

#### Example 218

A 20-mg (0.035-mmol) sample of  $\text{NiBr}_2[2\text{-NpCH=N(CH}_2)_3\text{N=CH-2-Np}]$ , where Np = naphthyl, (see structure below) was magnetically stirred under nitrogen in a 50-mL Schlenk flask with 25 mL of dry deaerated, toluene. Then 0.6 mL of polymethylalumoxane (3.3M) was injected; the light pink suspension became a dark gray-green solution, eventually with black precipitate. The mixture was immediately pressurized with ethylene to 7 psig and was stirred at 23°C for 18 hr, during which time the mixture became a clear yellow solution with black, sticky precipitate. The ethylene was vented; the offgas contained about 3% butenes (90:10 1-butene: trans-2-butene) by gas chromatography (30-m Quadrex GSQ® Megabore column; 50-250°C at 10°/min). The toluene solution was stirred with 6N HCl and methanol and was separated; concentration of the toluene solution followed by acetone rinsing the residue yielded 85 mg of liquid polyethylene. H-1 NMR ( $\text{CDCl}_3$ ) analysis: 209  $\text{CH}_3$ 's per 1000  $\text{CH}_2$ 's. This

Example demonstrates the efficacy of a catalyst with a bis-imine ligand in which the imine groups are not alpha to one another.



5

#### Example 219

A 17-mg (0.027-mmol) sample of [(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>]ZrCl<sub>4</sub> was magnetically stirred under nitrogen in a 50-mL Schlenk flask with 25 mL of dry, deaerated toluene. Then 0.6 mL of polymethylalumoxane (3.3M) was injected; the yellow suspension became an orange-yellow solution. The mixture was pressurized with ethylene to 7 psig and was stirred at 23°C for 20 hr, during which time polymer slowly accumulated on the stir bar and eventually rendered the solution unstirrable. The toluene solution was stirred with 6N HCl and methanol and was filtered to yield (after MeOH and acetone washing and air-drying) 1.01g of white, fluffy polyethylene. Differential scanning calorimetry exhibited a melting point of 131°C (124J/g). This example demonstrates the efficacy of a Zr(IV) catalyst bearing a diimine ligand.

15

20

#### Example 220

A 14-mg (0.024-mmol) sample of [(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>]TiCl<sub>4</sub> was magnetically stirred under nitrogen in a 50-mL Schlenk flask with 25 mL of dry, deaerated toluene (distilled from Na under N<sub>2</sub>). Then 0.6 mL of polymethylalumoxane (3.3M) was injected; the yellow suspension became a dark brown suspension with some precipitate. The mixture was pressurized with ethylene to 7 psig and was stirred at 23°C for 3 hr, during which time polymer accumulated and rendered the solution unstirrable. The toluene solution was stirred with 6N HCl and methanol and was filtered to yield, after MeOH and acetone washing and air-drying, 1.09g of

25

30

35

white, fluffy polyethylene. Differential scanning calorimetry exhibited a melting point of 131°C (161J/g). This example demonstrates the efficacy of a Ti(IV) catalyst bearing a diimine ligand.

5

Example 221

A 28-mg (0.046-mmol) sample of [(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>]CoBr<sub>2</sub> was magnetically stirred under nitrogen in a 50-mL Schlenk flask with 25 mL of dry, deaerated toluene. Then 0.5 mL of polymethylalumoxane (3.3M) was injected, resulting in a deep purple solution, and the mixture was pressurized immediately with ethylene to 7 psig and stirred at 23°C for 17 hr. The solution remained deep purple but developed some viscosity due to polymer. The ethylene was vented; the offgas contained 1.5%

1-butene by gas chromatography (30-m Quadrex GSQ® Megabore column; 50-250°C at 10°/min). The toluene solution was stirred with 6N HCl/methanol and was separated; concentration of the toluene solution yielded, after drying under high vacuum, 0.18g of elastomeric polyethylene. A film of polymer cast from chlorobenzene was stretchy with good elastic recovery. Differential scanning calorimetry: glass transition: -41°C; melting endotherm: 43°C (15J/g). This example demonstrates the efficacy of a cobalt (II) catalyst bearing a diimine ligand.

25

Example 222

A 35-mg (0.066-mmol) sample of [(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>]FeCl<sub>2</sub> was magnetically stirred under nitrogen in a 50-mL Schlenk flask with 25 mL of dry, deaerated toluene. Then 0.6 mL of polymethylalumoxane (3.3M) was injected; the deep purple-blue solution became a royal purple solution, which evolved to deep green-black over time. The mixture was immediately pressurized with ethylene to 7 psig and was stirred at 23°C for 70 hr, during which time the mixture became a pale green solution with black, sticky precipitate. The ethylene was vented; the toluene solution was

35

stirred with 6N HCl and methanol and was filtered to yield 90 mg of polyethylene.

Differential scanning calorimetry: melting endotherm: 128°C (84J/g). This example demonstrates the efficacy of a iron (II) catalyst bearing a diimine ligand.

#### Example 223

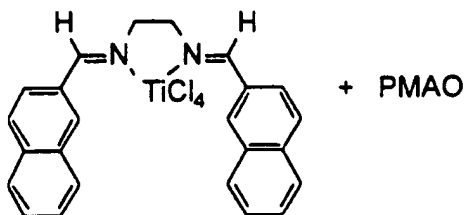
A mixture of 3.2g of the polyethylene product of Example 96, 60 mg (1.9 wt%) of dicumyl peroxide, and 50g (1.6 wt%) of triallylisocyanurate (TAIC) was dissolved in 100 mL of THF. The polymer was precipitated by stirring the solution in a blender with water; the peroxide and TAIC are presumed to have stayed in the polymer. The polymer was pressed into a clear, rubbery, stretchy film at 125°C. Strips of this film were subsequently pressed at various temperatures (100°C, 150°C, 175°C, 200°C) for various times (1 min, 5 min, 10 min) to effect peroxide-induced free-radical crosslinking. The cured sheets were all clear and stretchy and shorter-breaking: 100°C for 10 min gave no apparent cure, while 150°C/5 min seemed optimal. The cured films came closer to recovering their original dimensions than the uncured films. This example demonstrates peroxide curing of the amorphous elastomeric polyethylene.

#### Example 224

A 28-mg (0.050-mmol) sample of  $\text{TiCl}_4[2\text{-NpCH=N(CH}_2)_2\text{N=CH-2-Np}]$ , where Np = naphthyl, (see structure below) was magnetically stirred under nitrogen in a 50-mL Schlenk flask with 25 mL of dry, deaerated toluene. Then 0.6 mL of polymethylalumoxane (3.3M) was injected; the orange suspension became reddish-brown. The mixture was immediately pressurized with ethylene to 7 psig and was stirred at 23°C for 66 hr. The toluene solution was stirred with 6N HCl and methanol and was filtered to yield, after methanol washing and air-drying, 1.30g of white, fluffy polyethylene.

Differential scanning calorimetry: melting endotherm: 135°C (242J/g).

This example demonstrates the efficacy of a catalyst with a bis-imine ligand in which the imine groups are not alpha to one another.



#### Example 225

A 33-mg (0.053-mmol) sample of [(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>]ScCl<sub>3</sub>-THF was magnetically stirred under nitrogen in a 50-mL Schlenk flask with 25 mL of dry, deaerated toluene. Then 0.6 mL of polymethylalumoxane (3.3M) was injected; the pale orange solution became bright yellow. The mixture was immediately pressurized with ethylene to 7 psig and was stirred at 23°C for 17 hr, during which time the mixture remained yellow and granular suspended polymer appeared. The ethylene was vented; the toluene solution was stirred with 6N HCl and methanol and was filtered to yield 2.77g of white, granular polyethylene. This example demonstrates the efficacy of a scandium (III) catalyst bearing a diimine ligand.

#### Example 226

##### (2-t-BuPh)<sub>2</sub>DABAN

This compound was made by a procedure similar to that of Example 25. Three mL (19.2 mmol) of 2-t-butylaniline and 1.71 g (9.39 mmol) of acenaphthenequinone were partially dissolved in 50 mL of methanol (acenaphthenequinone was not completely soluble). An orange product was crystallized from CH<sub>2</sub>Cl<sub>2</sub> (3.51 g, 84.1%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz) δ 7.85 (d, 2H, J = 8.0 Hz, BIAN: Hp), 7.52 (m, 2H, Ar: Hm), 7.35 (dd, 2H, J = 8.0, 7.3 Hz, BIAN: Hm), 7.21 (m, 4H,

Ar: Hm and Hp), 6.92 (m, 2H, Ar: Ho), 6.81 (d, 2H, J = 6.9 Hz, BIAN: Ho), 1.38 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>).

#### Example 227

Methyl vinyl ketone was stirred over anhydrous K<sub>2</sub>CO<sub>3</sub> and vacuum transferred on a high vacuum line to a dry flask containing phenothiazine (50 ppm). Ethylene and methyl vinyl ketone (5 ml) were copolymerized according to Example 16 using catalyst {[(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>] PdCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C(O)OCH<sub>3</sub>}<sup>+</sup>SbF<sub>6</sub><sup>-</sup> (0.084 g, 0.10 mmol) to give 0.46 g copolymer (0.38 g after correcting for catalyst residue). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 0.75-0.95(m, CH<sub>3</sub>); 0.95-1.45(m, CH and CH<sub>2</sub>); 1.55(m, -CH<sub>2</sub>CH<sub>2</sub>C(O)CH<sub>3</sub>); 2.15(s, -CH<sub>2</sub>CH<sub>2</sub>C(O)CH<sub>3</sub>); 2.4(t, -CH<sub>2</sub>CH<sub>2</sub>C(O)CH<sub>3</sub>). Based on the triplet at 2.15, it appears that much of the ketone functionality is located on the ends of hydrocarbon branches. Integration shows that the copolymer contains 2.1 mole% methyl vinyl ketone, and 94 methyl carbons (exclusive of methyl ketones) per 1000 methylene carbons. The turnover numbers are 128 equivalents of ethylene and 3 equivalents of methyl vinyl ketone per Pd. GPC (THF, PMMA standard): Mn=5360 Mw=7470 Mw/Mn = 1.39.

#### Example 228

A Schlenk flask containing 122 mg (0.0946 mmol) of {[(4-MePh)<sub>2</sub>DABMe<sub>2</sub>]PdMe(N≡CMe)}<sup>+</sup>BAF<sup>-</sup> was placed under a CO atmosphere. The yellow powder turned orange upon addition of CO, and subsequent addition of 20 mL of CH<sub>2</sub>Cl<sub>2</sub> resulted in the formation of a clear red solution. t-Butylstyrene (10 mL) was added next and the resulting orange solution was stirred for 25.7 h at room temperature. The solution was then added to methanol in order to precipitate the polymer, which was collected by filtration and dried in a vacuum oven at 50 °C overnight (yield = 4.03 g): GPC Analysis (THF, polystyrene standards): M<sub>w</sub> = 8,212; M<sub>n</sub> = 4,603; PDI = 1.78. The <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of the isolated polymer was consistent with a mixture of copolymer and poly(t-butylstyrene).

Mixtures of alternating copolymer and poly(*t*-butylstyrene) were obtained from this and the following polymerizations and were separated by extraction of the homopolymer with petroleum ether. When R<sup>2</sup> and R<sup>5</sup> were 4-MePh (this example) atactic alternating copolymer was isolated. When R<sup>2</sup> and R<sup>5</sup> were 2,6-*i*-PrPh (Example 229) predominantly syndiotactic alternating copolymer was isolated. (Spectroscopic data for atactic, syndiotactic, and isotactic *t*-butylstyrene/CO alternating copolymers has been reported: M. Brookhart, et al., *J. Am. Chem. Soc.* 1992, 114, 5894-5895; M. Brookhart, et al., *J. Am. Chem. Soc.* 1994, 116, 3641-3642.)

Petroleum ether (~200 mL) was added to the polymer mixture in order to extract the homopolymer, and the resulting suspension was stirred vigorously for several h. The suspension was allowed to settle, and the petroleum ether solution was decanted off of the gray powder. The powder was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and the resulting solution was filtered through Celite. The CH<sub>2</sub>Cl<sub>2</sub> was then removed and the light gray powder (0.61 g) was dried in vacuo. <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic data are consistent with the isolation of atactic alternating copolymer: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 7.6 - 6.2 (br envelope, 4, H<sub>Ar1</sub>), 4.05 and 3.91 (br, 1, CH<sub>Ar'</sub>), 3.12 and 2.62 (br, 2, CH<sub>2</sub>), 1.26-1.22 (br envelope, 9, CMe<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 207.5 - 206.0 (br envelope, -C(O)-), 150.0 - 149.0 (br, Ar': C<sub>p</sub>), 135.0 - 133.8 (br envelope, Ar': C<sub>ipso</sub>), 127.9 (Ar': C<sub>m</sub>), 126.0 - 125.0 (br, Ar': C<sub>o</sub>), 53.0 - 51.0 (br envelope, CH<sub>Ar'</sub>), 46.0 - 42.0 (br envelope, CH<sub>2</sub>), 34.3 (CMe<sub>3</sub>), 31.3 (CMe<sub>3</sub>).

#### Example 229

The procedure of Example 228 was followed using 134 mg (0.102 mmol) [(2,6-*i*-PrPh)<sub>2</sub>DABMe<sub>2</sub>]PdMe(N=CMe)}\*BAF<sup>-</sup>. A mixture (2.47 g) of copolymer and poly(*t*-butylstyrene) was isolated. GPC Analysis (THF, polystyrene standards): M<sub>w</sub> = 10,135; M<sub>n</sub> = 4,922; PDI =



2.06. Following the extraction of the homopolymer with petroleum ether, 0.49 g of off-white powder was isolated.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopic data are consistent with the isolation of predominantly syndiotactic copolymer, although minor resonances are present:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  7.20 (d, 2,  $J$  = 8.14,  $\text{Ar}'$ :  $\text{H}_o$  or  $\text{H}_m$ ), 6.87 (d, 2,  $J$  = 7.94,  $\text{Ar}'$ :  $\text{H}_o$  or  $\text{H}_m$ ), 3.91 (dd, 1,  $J$  = 9.06, 3.16,  $\text{CHAr}'$ ), 3.15 (dd, 1,  $J$  = 18.02, 9.96,  $\text{CHH}'$ ), 2.65 (dd, 1,  $J$  = 17.90,  $\text{CHH}'$ ), 1.25 (s, 9,  $\text{CMe}_3$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  207.0 ( $-\text{C}(\text{O})-$ ), 149.8 ( $\text{Ar}'$ :  $\text{C}_p$ ), 134.5 ( $\text{Ar}'$ :  $\text{C}_{ipso}$ ), 127.8 ( $\text{Ar}'$ :  $\text{C}_m$ ), 125.6 ( $\text{Ar}'$ :  $\text{C}_o$ ), 51.7 ( $\text{CHAr}'$ ), 45.6 ( $\text{CH}_2$ ), 34.3 ( $\text{CMe}_3$ ), 31.3 ( $\text{CMe}_3$ ).

#### Example 230

A Schlenk flask containing 74.3 mg (0.0508 mmol) of  $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdMe}(\text{OEt}_2)\}^+\text{BAF}^-$  was evacuated, cooled to  $-78^\circ\text{C}$  and then placed under an atmosphere of ethylene/CO (1:1 mixture). Following the addition of 50 mL of chlorobenzene, the reaction mixture was allowed to warm to room temperature and stirred. A small amount of white precipitate appeared on the sides of the flask after 0.5 h and more precipitate formed during the next two days. After stirring for 47.2 h, the reaction mixture was added to methanol and the resulting suspension was stirred. The precipitate was then allowed to settle, and the methanol was decanted, leaving behind a cream powder (0.68 g), which was dried in a vacuum oven at  $70^\circ\text{C}$  for one day.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopic data are consistent with the isolation of an alternating copolymer of ethylene and carbon monoxide:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ /pentafluorophenol, 400 MHz)  $\delta$  2.89 ( $-\text{C}(\text{O})-\text{CH}_2\text{CH}_2-\text{C}(\text{O})-$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ /pentafluorophenol, 100 MHz)  $\delta$  212.1 ( $-\text{C}(\text{O})-$ ), 35.94 ( $\text{CH}_2$ ).

For comparisons of the spectroscopic data of alternating E/CO copolymers herein with literature values, see for example: E. Drent, et al., *J. Organomet. Chem.* 1991, 417, 235-251.

Example 231

A Schlenk flask containing 73.2 mg (0.0500 mmol) of  $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdMe}(\text{OEt}_2)\}^+\text{BAF}^-$  was evacuated, cooled to  $-78\text{ }^\circ\text{C}$ , and then back-filled with ethylene (1 atm). Chlorobenzene (50 mL) was added via syringe and the solution was allowed to warm to room temperature. After 0.5 h, the reaction vessel was very warm and ethylene was being rapidly consumed. The reaction flask was then placed in a room-temperature water bath and stirring was continued for a total of 3 h. A very viscous solution formed. The atmosphere was then switched to ethylene/carbon monoxide (1:1 mixture, 1 atm) and the reaction mixture was stirred for 47.7 more hours. During this time, the solution became slightly more viscous. The polymer was then precipitated by adding the chlorobenzene solution to methanol. The methanol was decanted off of the polymer, which was then partially dissolved in a mixture of  $\text{Et}_2\text{O}$ ,  $\text{CH}_2\text{Cl}_2$  and THF. The insoluble polymer fraction (2.71 g) was collected on a sintered glass frit, washed with chloroform, and then dried in a vacuum oven at  $70\text{ }^\circ\text{C}$  for 12 h. The NMR spectroscopic data of the gray rubbery material are consistent with the formation of a diblock of branched polyethylene and linear poly(ethylene-carbon monoxide):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ /pentafluorophenol, 400 MHz)  $\delta$  2.85 ( $-\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{C}(\text{O})-$ ), 2.77 ( $-\text{C}(\text{O})\text{CH}_2$ , minor), 1.24 ( $\text{CH}_2$ ), 0.83 ( $\text{CH}_3$ ); Polyethylene Block Branching:  $\sim 103\text{ CH}_3$  per 1000  $\text{CH}_2$ ; Relative Block Length  $[(\text{CH}_2\text{CH}_2)_n - (\text{C}(\text{O})\text{CH}_2\text{CH}_2)_m]$ :  $n/m = 2.0$ .  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ /pentafluorophenol, 100 MHz; data for ethylene-CO block)  $\delta$  211.6 ( $-\text{C}(\text{O})-$ ), 211.5 ( $-\text{C}(\text{O})-$ , minor), 35.9 ( $\text{C}(\text{O})-\text{CH}_2\text{CH}_2-\text{C}(\text{O})$ ), 35.8 ( $\text{C}(\text{O})\text{CH}_2$ , minor).

Example 232

A Schlenk flask containing 75.7 mg (0.0527 mmol) of  $\{[(2,6\text{-}i\text{-PrPh})_2\text{DABH}_2]\text{PdMe}(\text{OEt}_2)\}^+\text{BAF}^-$  was evacuated, cooled to  $-78\text{ }^\circ\text{C}$ , and then back-filled with ethylene (1 atm). Chlorobenzene (50 mL) was added via syringe, the solution was allowed to warm to room temperature and stirred for 3 h. The solution did not become warm or viscous during this time. The atmosphere was changed to ethylene/carbon monoxide (1:1 mixture, 1 atm) and the solution was stirred for 47.7 more hours. During this time, the reaction mixture became quite viscous and solvent-swollen polymer precipitated on the sides of the flask. The polymer was precipitated by addition of the reaction mixture to methanol. The methanol was decanted off of the rubbery polymer (4.17 g), which was then dried in a vacuum oven for one day at  $70\text{ }^\circ\text{C}$ . Chloroform was then added to the polymer and the rubbery insoluble fraction (0.80 g) was collected on a sintered glass frit. A  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 400 MHz) of the chloroform-soluble polymer showed no carbon monoxide incorporation; only branched polyethylene was observed. NMR spectroscopic data for the chloroform-insoluble fraction was consistent with the formation of a diblock of branched polyethylene and linear poly(ethylene-carbon monoxide):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ /pentafluorophenol, 400 MHz)  $\delta$  2.88 ( $\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{C}(\text{O})$ ), 1.23 ( $\text{CH}_2$ ), 0.83 ( $\text{CH}_3$ ); Polyethylene Block Branching: 132  $\text{CH}_3$  per 1000  $\text{CH}_2$ ; Relative Block Length  $[(\text{CH}_2\text{CH}_2)_n - (\text{C}(\text{O})\text{CH}_2\text{CH}_2)_m]: n/m = 0.30$ ;  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ /pentafluorophenol, 100 MHz; data for ethylene-CO block)  $\delta$  211.3 ( $-\text{C}(\text{O})-$ ), 211.3 ( $-\text{C}(\text{O})-$ , minor), 36.5 ( $-\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{C}(\text{O})-$ ), 36.4 ( $\text{C}(\text{O})\text{CH}_2$ , minor).

Example 233

A 34-mg (0.053-mmol) sample of the crude product of Example 235, was magnetically stirred under nitrogen in a 50-mL Schlenk flask with 25 mL of dry, deaerated toluene. Then 0.6 mL of polymethylalumoxane (3.3M) was injected; the purple-pink suspension became a gold-

green solution with black precipitate. The mixture was pressurized with ethylene to 152 kPa (absolute) and was stirred for 20 hr. Within the first hour, polymer was observed to be accumulating on the stir bar and the walls of the flask. The ethylene was vented and the toluene solution was stirred with 6N HCl and methanol and was filtered to yield (after MeOH and acetone washing and air-drying) 1.37g of white, granular polyethylene. This example demonstrates the efficacy of a catalyst with a 1,3-diimine ligand.

Example 234

Synthesis of MeC(=N-2,6-C<sub>6</sub>H<sub>3</sub>-iPr<sub>2</sub>)CH=C(NH-2,6-C<sub>6</sub>H<sub>3</sub>-iPr<sub>2</sub>)Me

Concentrated HCl (0.3 ml, 3.6 mmol) was added to a solution of 2,4-pentanedione (1.2 g, 12 mmol) and 2,6-diisopropylaniline (5.0 ml, 26.6 mmol) in 15 ml ethanol. The reaction mixture was refluxed for 21 h during which time a white solid precipitated. This was separated by filtration, dried under vacuum and treated with saturated aqueous sodium bicarbonate. The product was extracted with methylene chloride, and the organic layer dried over anhydrous sodium sulfate. Removal of the solvent afforded 1.43 g (28%) of the title compound as a white crystalline product; mp: 140-142°C; <sup>1</sup>H NMR: (CDCl<sub>3</sub>) δ 12.12 (bs, 1 H, NH), 7.12 (m, 6 H, aromatic), 4.84 (s, 1 H, C=CH-C), 3.10 (m, 4 H, isopropyl CH, J = 7 Hz), 1.72 (s, 6 H, CH<sub>3</sub>), 1.22 (d, 12 H, isopropyl CH<sub>3</sub>, J = 7 Hz), 1.12 (d, 12 H, isopropyl CH<sub>3</sub>, J = 7 Hz). <sup>13</sup>C NMR: (CDCl<sub>3</sub>) δ 161.36 (C=N), 142.63 (aromatic C-1), 140.89 (aromatic C-2), 125.27 (aromatic C-4), 123.21 (aromatic C-3), 93.41 (-CH=), 28.43 (isopropyl CH), 24.49 (isopropyl CH<sub>3</sub>), 23.44 (isopropyl CH<sub>3</sub>), 21.02 (CH<sub>3</sub>). MS: m/z = 418.333 (calc. 418.335).

## Example 235

Synthesis of an ethylene polymerization catalyst  
from Ni(MeOCH<sub>2</sub>CH<sub>2</sub>OMe)Br<sub>2</sub> and MeC(=N-2,6-C<sub>6</sub>H<sub>3</sub>-  
iPr<sub>2</sub>)CH=C(NH-2,6-C<sub>6</sub>H<sub>3</sub>-iPr<sub>2</sub>)Me

5 Ni(MeOCH<sub>2</sub>CH<sub>2</sub>OMe)Br<sub>2</sub> (0.110 g, 0.356 mmol) and  
MeC(=N-2,6-C<sub>6</sub>H<sub>3</sub>-iPr<sub>2</sub>)CH=C(NH-C<sub>6</sub>H<sub>3</sub>-iPr<sub>2</sub>)Me (0.150 g,  
0.359 mmol) were combined in 10 mL of methylene  
chloride to give a peach-colored suspension. The  
reaction mixture was stirred at room temperature  
10 overnight, during which time a lavender-colored powder  
precipitated. This was isolated by filtration, washed  
with petroleum ether and dried affording 0.173 g of  
material. This compound was used as the catalyst in  
Example 233.

15

## Example 236

{[(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>]Pd(MeCN)<sub>2</sub>}(BF<sub>4</sub>)<sub>2</sub>

[Pd(MeCN)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub> (0.423 g, 0.952 mmol) and (2,6-  
i-PrPh)<sub>2</sub>DABMe<sub>2</sub> (0.385 g, 0.951 mmol) were dissolved in  
30 mL acetonitrile under nitrogen to give an orange  
20 solution. The reaction mixture was stirred at room  
temperature overnight; it was then concentrated in  
vacuo to afford a yellow powder. Recrystallization  
from methylene chloride/petroleum ether at -40°C  
afforded 0.63 g of the title compound as a yellow  
25 crystalline solid. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 7.51 (t, 2H,  
H<sub>para</sub>), 7.34 (d, 4H, H<sub>meta</sub>), 3.22 (sept, 4H, CHMe<sub>2</sub>),  
2.52 (s, 6H, N=CMe), 1.95 (s, 6H, NC=Me), 1.49 (d, 12H,  
CHMe<sub>2</sub>), 1.31 (d, 12H, CHMe<sub>2</sub>).

## Example 237

30

Ethylene Polymerization Catalyzed by {[(2,6-i-  
PrPh)<sub>2</sub>DABMe<sub>2</sub>]Pd(MeCN)<sub>2</sub>}(BF<sub>4</sub>)<sub>2</sub>

A 100 mL autoclave was charged with a solution of  
{[(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>]Pd(MeCN)<sub>2</sub>}(BF<sub>4</sub>)<sub>2</sub> (0.043 g, 0.056  
mmol) dissolved in 50 mL chloroform and ethylene (2.8  
35 MPa). The reaction mixture was stirred under 2.8 MPa  
ethylene for 9 h 15 min. During this time, the  
temperature inside the reactor increased from 23 to  
27°C. The ethylene pressure was then vented and

Volatiles removed from the reaction mixture to afford 1.65 g of a viscous yellow oil. This was shown by  $^1\text{H}$  NMR to be branched polyethylene containing 94 methyl-ended branches per 1000 methylenes.

5

Example 238Ethylene polymerization by  $\text{Ni}(\text{COD})_2/(2,6\text{-i-PrPh})_2\text{DABMe}_2\cdot\text{HBAF}(\text{Et}_2\text{O})_2$ 

$\text{Ni}(\text{COD})_2$  (0.017 g, 0.06 mmol) and (2,6-i-PrPh) $_2$ DABMe $_2\cdot\text{HBAF}(\text{Et}_2\text{O})_2$  (0.085 g, 0.06 mmol) were dissolved in 5 mL of benzene under nitrogen at room temperature. The resulting solution was quickly frozen, and then allowed to thaw under 6.9 MPa of ethylene at 50°C. The reaction mixture was agitated under these conditions for 18 h affording a solvent swelled polymer. Drying afforded 5.8 g of a polyethylene as a tough, rubbery material.

10

15

Example 239Ethylene polymerization by  $\text{Pd}_2(\text{dba})_3$  (dba = dibenzylideneacetone) / (2,6-i-PrPh) $_2$ DABMe $_2\cdot\text{HBAF}(\text{Et}_2\text{O})_2$ 

A sample of (Et $_2$ O)HBAF (200 mg, 0.20 mmol) was dissolved in 10 mL of Et $_2$ O. To this solution was added 1 equivalent of DABMe $_2$  (or other  $\alpha$ -diimine). The solution became red. Removal of the volatiles in vacuo gave a red solid of the acid- $\alpha$ -diimine complex.

20

$\text{Pd}_2(\text{dba})_3$  (0.054 g, 0.06 mmol) and (2,6-i-PrPh) $_2$ DABMe $_2\cdot\text{HBAF}(\text{Et}_2\text{O})_2$  (0.076 g, 0.05 mmol) were dissolved in 5 mL of benzene under nitrogen at room temperature. The resulting solution was agitated under 6.9 MPa of ethylene at 50°C for 18 h. The product mixture was concentrated to dryness in vacuo, affording an extremely viscous oil.  $^1\text{H}$  NMR showed the product to be branched polyethylene containing 105 methyl ended branches per 1000 methylenes.

25

30

Example 240

Toluene (30 mL), 4-vinylcyclohexene (15 mL), and 20 mg of [(2,6-i-PrPh) $_2$ DABH $_2$ ]NiBr $_2$  (0.03 mmol) were combined in a Schlenk flask under an atmosphere of ethylene. A 10 % MAO solution (3 mL) in toluene was

35

added. The resulting purple solution was stirred for 16 h. After only a few hours, polymer began to precipitate and adhere to the walls of the flask. The polymerization was quenched and the polymer precipitated from acetone. The polymer was dried in vacuo overnight resulting in 100 mg of a white solid. Characterization by proton NMR suggests incorporation of 4-vinylcyclohexene as a comonomer.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.64 (m, vinyl, cyclohexene), 2.0-0.9 (overlapping m, including cyclohexyl methylene, methylene (PE), methine), 0.78 (methyl, PE). There are also some minor signals in the base line that suggests incorporation of the internal olefin (cyclohexene) and free  $\alpha$ -olefin (4-vinyl).

Example 241

The catalyst  $\{[(2,6\text{-}i\text{-PrPh})_2\text{DABMe}_2]\text{PdCH}_2\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OCH}_3\}\text{SbF}_6^-$  (1.703 g, 2 mmol) was added to a 1 gal Hastalloy® autoclave. The autoclave was sealed, flushed with nitrogen and then charged with 1500 g of  $\text{SO}_2$ . An over pressure of 3.5 MPa of ethylene was maintained for 24 hr at  $25^\circ\text{C}$ . The autoclave was vented to relieve the pressure and the contents of the autoclave were transferred to a jar. The polymer was taken up in methylene chloride and purified by precipitation into excess acetone. The precipitated polymer was dried in vacuo to give 2.77 g of polymer. The polymer displayed strong bands attributable to sulfonyl group in the infrared (film on KBr plate) at 1160 and  $1330\text{ cm}^{-1}$ .

Example 242

Copolymerization of Ethylene and Methyl Vinyl Ketone

Methyl vinyl ketone (MVK) was stirred over anhydrous  $\text{K}_2\text{CO}_3$  and vacuum transferred using a high vacuum line to a dry flask containing phenothiazine (50 ppm). Ethylene and MVK (5 ml) were copolymerized using the procedure of Example 125 using as catalyst  $\{[(2,6\text{-}i\text{-PrPh})_2\text{DABMe}_2]\text{PdCH}_2\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OCH}_3\}\text{SbF}_6^-$  (0.084 g, 0.10

..mmol) to give 0.46 g of copolymer (0.38 g after correcting for catalyst residue).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 0.75-0.95 (m,  $\text{CH}_3$ ); 0.95-1.45 (m, CH and  $\text{CH}_2$ ); 1.55 (m,  $-\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{CH}_3$ ); 2.15 (s,  $-\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{CH}_3$ ); 2.4 (t,  $-\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{CH}_3$ ). Based on the triplet at 2.15, it appeared that much of the ketone functionality was located on the ends of the hydrocarbon branches. Integration showed that the copolymer contained 2.1 mole% MVK, and has 94 methyl carbon (exclusive of methyl ketones) per 1000 methyl carbon atoms. The turnover was 128 equivalents of ethylene and 3 equivalents of MVK per Pd. GPC (THF, PMMA standard):  $M_n=5360$ ,  $M_w=7470$ ,  $M_w/M_n=1.39$ .

#### Example 243

15 1-Hexene (20 ml) was polymerized in methylene chloride (10 ml) according to example 173 to give 4.22 g of viscous gel (1002 equivalents 1-hexene per Pd). Integration of the  $^1\text{H}$  NMR spectrum showed 95 methyl carbons per 1000 methylene carbons.  $^{13}\text{C}$  NMR  
20 quantitative analysis, branching per 1000  $\text{CH}_2$ : Total methyls (103), Methyl (74.9), Ethyl (none detected), Propyl (none detected), Butyl (12.4), Amyl (none detected),  $\geq$ Hexyl and end of chains (18.1). Integration of the  $\text{CH}_2$  peaks due to the structure -  
25  $\text{CH}(\text{R})\text{CH}_2\text{CH}(\text{R}')-$ , where R is an alkyl group, and R' is an alkyl group with two or more carbons showed that in 74% of these structures, R = Me.

Listed below are the  $^{13}\text{C}$  NMR data upon which the above analysis is based.



$^{13}\text{C}$  NMR data

TCB, 140C, 0.05M CrAcAc

<u>Freq ppm</u>	<u>Intensity</u>	
42.6359	4.05957	$\alpha\alpha$ for Me & Et <sup>+</sup> branches
37.8987	9.10141	$\text{MB}_3^+$
37.2833	64.4719	$\alpha\text{B}_1$
36.8537	8.67514	
35.5381	4.48108	
34.8803	4.30359	
34.5514	5.20522	
34.2755	21.6482	
33.2411	4.13499	$\text{MB}_1$
32.9811	32.0944	$\text{MB}_1$
31.9467	14.0714	$3\text{B}_6^+, 3\text{EOC}$
30.7212	5.48503	$\gamma+\gamma+\text{B}, 3\text{B}_4$
30.2597	28.5961	$\gamma+\gamma+\text{B}, 3\text{B}_4$
30.143	50.4726	$\gamma+\gamma+\text{B}, 3\text{B}_4$
29.7717	248	$\gamma+\gamma+\text{B}, 3\text{B}_4$
29.342	17.4732	$\gamma+\gamma+\text{B}, 3\text{B}_4$
27.5702	27.2867	$\beta\gamma$ for 2 Me branches
27.1935	49.5612	$\beta\gamma+\text{B}, (4\text{B}_5, \text{etc.})$
27.045	23.1776	
23.0292	9.56673	$2\text{B}_4$
22.6526	14.1631	$2\text{B}_5^+, 2\text{EOC}$
20.2495	5.72164	$1\text{B}_1$
19.7455	48.8451	$1\text{B}_1$
13.9049	21.5008	$1\text{B}_4^+, 1\text{EOC}$

Example 244

- 5        1-Heptene (20 ml) was polymerized in methylene chloride (10 ml) according to example 173 to give 1.29 g of viscous gel (263 equivalents 1-heptene per Pd). Integration of the  $^1\text{H}$  NMR spectrum showed 82 methyl carbons per 1000 methylene carbons.  $^{13}\text{C}$  NMR
- 10    quantitative analysis, branching per 1000  $\text{CH}_2$ : Total methyls (85), Methyl (58.5), Ethyl (none detected), Propyl (none detected), Butyl (none detected), Amyl (14.1),  $\geq$ Hexyl and end of chains (11.1). Integration of the  $\text{CH}_2$  peaks due to the structure  $-\text{CH}(\text{R})\text{CH}_2\text{CH}(\text{R}')-$
- 15    , where R is an alkyl group, and R' is an alkyl group with two or more carbons showed that in 71% of these structures, R = Me. DSC (two heats,  $-150 \rightarrow 150^\circ\text{C}$ ,  $15^\circ\text{C}/\text{min}$ ) shows  $T_g = -42^\circ\text{C}$  and a  $T_m = 28^\circ\text{C}$  (45 J/g).
- 20        Listed below are the  $^{13}\text{C}$  NMR data upon which the above analysis is based.

<sup>13</sup>C NMR data

TCB, 120C, 0.05M CrAcAc

<u>Freq ppm</u>	<u>Intensity</u>	
42.6041	5.16375	αα for Me & Et <sup>+</sup>
37.851	15.9779	MB <sub>3</sub> <sup>+</sup>
37.5963	7.67322	
37.2356	99.6734	αB <sub>1</sub>
35.4956	7.58713	
34.8219	6.32649	
34.6097	6.37695	
34.2278	37.6181	
33.3418	3.78275	MB <sub>1</sub>
32.9228	60.7999	MB <sub>1</sub>
32.2809	13.6249	
31.9148	21.2367	3B <sub>6</sub> <sup>+</sup> , 3EOC
30.5886	13.8482	γ+γ+B, 3B <sub>4</sub>
30.4613	22.1996	γ+γ+B, 3B <sub>4</sub>
30.2173	48.8725	γ+γ+B, 3B <sub>4</sub>
30.1059	80.2189	γ+γ+B, 3B <sub>4</sub>
29.7292	496	γ+γ+B, 3B <sub>4</sub>
29.3049	26.4277	γ+γ+B, 3B <sub>4</sub>
27.1511	114.228	βγ <sup>+</sup> B <sub>1</sub> (4B <sub>5</sub> , etc.)
27.0025	47.5199	
26.7267	20.4817	
24.5623	3.32234	
22.6207	36.4547	2B <sub>5</sub> <sup>+</sup> , 2EOC
20.2176	7.99554	1B <sub>1</sub>
19.7084	70.3654	1B <sub>1</sub>
13.8677	36.1098	1B <sub>4</sub> <sup>+</sup> , EOC

Example 245

- 5 1-Tetradecene (20 ml) was polymerized in methylene chloride (10 ml) according to example 173 to give 6.11 g of sticky solid (622 equivalents 1-tetradecene per Pd). Integration of the <sup>1</sup>H NMR spectrum showed 64 methyl carbons per 1000 methylene carbons. <sup>13</sup>C NMR
- 10 quantitative analysis, branching per 1000 CH<sub>2</sub>: Total methyls (66), Methyl (35.2), Ethyl (5.6), Propyl (1.2), Butyl (none detected), Amyl (2.1),

- ≥Hexyl and end of chains (22.8). Integration of the CH<sub>2</sub> peaks due to the structure -CH(R)CH<sub>2</sub>CH(R')- ,
- 15 where R is an alkyl group, and R' is an alkyl group with two or more carbons showed that in 91% of these structures, R = Me. The region integrated for the structure where both R and R' are ≥Ethyl was 40.0 ppm to 41.9 ppm to avoid including a methine carbon
- 20 interference.

Listed below are the  $^{13}\text{C}$  NMR data upon which the above analysis is based.

 $^{13}\text{C}$  NMR data

TCB, 120C, 0.05M CrAcAc

<u>Freq ppm</u>	<u>Intensity</u>	
39.2826	6.684	$\text{MB}_2$
37.8012	8.13042	$\text{MB}_3^+$
37.2171	24.8352	$\alpha\text{B}_1, 3\text{B}_3$
34.1694	31.5295	$\alpha\gamma^+\text{B}, (4\text{B}_4, 5\text{B}_5, \text{etc.}) \text{MB}_1$
33.6809	13.0926	$\alpha\gamma^+\text{B}, (4\text{B}_4, 5\text{B}_5, \text{etc.}) \text{MB}_1$
32.9004	13.0253	$\text{MB}_1$
31.9022	25.0187	$3\text{B}_6^+, 3\text{EOC}$
30.1978	42.5593	$\gamma+\gamma^+\text{B}, 3\text{B}_4$
30.0969	34.1982	$\gamma+\gamma^+\text{B}, 3\text{B}_4$
29.7252	248	$\gamma+\gamma^+\text{B}, 3\text{B}_4$
29.3004	26.4627	$\gamma+\gamma^+\text{B}, 3\text{B}_4$
27.1394	31.8895	$\beta\gamma^+\text{B}, 2\text{B}_2, (4\text{B}_5, \text{etc.})$
26.9748	40.5922	$\beta\gamma^+\text{B}, 2\text{B}_2, (4\text{B}_5, \text{etc.})$
26.3642	7.06865	$\beta\gamma^+\text{B}, 2\text{B}_2, (4\text{B}_5, \text{etc.})$
22.6209	25.5043	$2\text{B}_5^+, 2\text{EOC}$
19.6952	15.0868	$1\text{B}_1$
13.8759	24.9075	$1\text{B}_4^+, 1\text{EOC}$
10.929	7.63831	$1\text{B}_2$

5

Example 246

This example demonstrates copolymerization of ethylene and 1-octene to give polymer with mostly C6+ branches. Under nitrogen,  $[(2,6\text{-i-PrPh})_2\text{DABH}_2]\text{NiBr}_2$  (0.005 g, 0.0084 mmol) and 9.6 wt. % MAO in toluene (0.50 mL) were dissolved in 10 mL of toluene at room temperature. The resulting solution was immediately transferred to a 100 mL autoclave that had previously been flushed with nitrogen and evacuated. 1-Octene (40 mL, 255 mmol) was then added to the reactor, which was subsequently charged with ethylene (320 kPa). The reaction mixture was stirred for 60 min, during which time the temperature inside the reactor varied between 24 and 28°C. Ethylene was then vented, and the product polymer was precipitated by addition of the crude reaction mixture to 50 mL of methanol containing 5 mL of concentrated aqueous HCl. The polymer precipitated as a slightly viscous oil; this was removed by pipette and dried affording 3.03 g of amorphous ethylene/1-octene copolymer. Branching per 1000  $\text{CH}_2$  was

- quantified by  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_3\text{Cl}_3$ ,  $25^\circ\text{C}$ ): total Methyls (83.6), Methyl (4), Ethyl (1.6), Propyl (4.4), Butyl (5.6), Amyl (10.1),  $\geq\text{Hex}$  and end of chains (65.8),  $\geq\text{Am}$  and end of chains (69.3),  $\geq\text{Bu}$  and end of chains (73.7).
- 5 GPC (trichlorobenzene vs. linear polyethylene):  $M_w = 48,200$ ,  $M_n = 17,000$ . DSC:  $T_g = -63^\circ\text{C}$ .

#### Example 247

- This example demonstrates copolymerization of ethylene and 1-octene to give polymer with mostly
- 10 methyl and  $\text{C}_6+$  branches. Under nitrogen, [(2,6-i-PrPh) $_2$ DABH $_2$ ] $\text{NiBr}_2$  (0.005 g, 0.0084 mmol) and 9.6 wt. % MAO in toluene (0.50 mL) were dissolved in 40 mL of toluene at  $-40^\circ\text{C}$ . The resulting solution was immediately transferred to a 100 mL autoclave that had
- 15 previously been flushed with nitrogen and evacuated. 1-Octene (10 mL, 64 mmol) was then added to the reactor under 324 kPa of ethylene. The resulting reaction mixture was stirred under 324 kPa of ethylene for 1 h 10 min. During this time the temperature inside the
- 20 reactor varied between 29 and  $40^\circ\text{C}$ . Ethylene was then vented, and the product polymer was precipitated by addition of the crude reaction mixture to methanol. The polymer was dried affording 6.45 g of ethylene/1-octene copolymer. Branching per 1000  $\text{CH}_2$  was
- 25 quantified by  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_3\text{Cl}_3$ ,  $25^\circ\text{C}$ ): Total methyls (50.7), Methyl (13.7), Ethyl (2.4), Propyl (3.5), Butyl (4.1), Amyl (1),  $\geq\text{Hex}$  and end of chains (26),  $\geq\text{Am}$  and end of chains (30.4),  $\geq\text{Bu}$  and end of chains (31). GPC (trichlorobenzene vs. linear polyethylene):  $M_w =$
- 30 116,000,  $M_n = 9,570$ .

#### Example 248

- Under a nitrogen atmosphere,  $\text{Ni}(\text{COD})_2$  (0.017 g, 0.06 mmol) and (2,6-i-PrPh) $_2$ DABMe $_2$  (0.024 g, 0.06 mmol) were dissolved in benzene (5.0 mL). To the resulting
- 35 solution was added HBAF $\cdot$ (Et $_2\text{O}$ ) $_2$  (0.060 g, 0.06 mmol). The resulting solution was immediately frozen inside a 40 mL shaker tube glass insert. The glass insert was transferred to a shaker tube, and its contents allowed

to thaw under an ethylene atmosphere. The reaction mixture was agitated under 6.9 MPa C<sub>2</sub>H<sub>4</sub> for 17.5 h at ambient temperature. The final reaction mixture contained polyethylene, which was washed with methanol and dried; yield of polymer = 9.2 g. <sup>1</sup>H NMR (CDCl<sub>2</sub>CDCl<sub>2</sub>, 120°C) showed that this sample contained 49 methyl-ended branches per 1000 methylenes. DSC: T<sub>m</sub> = 118.8°C, ΔH<sub>f</sub> = 87.0 J/g.

#### Example 249

Under a nitrogen atmosphere, Ni[P(O-2-C<sub>6</sub>H<sub>4</sub>-Me)<sub>3</sub>]<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>) (0.047 g, 0.06 mmol) and (2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub> (0.024 g, 0.06 mmol) were dissolved in benzene (5.0 mL). To the resulting solution was added HBAF·(Et<sub>2</sub>O)<sub>2</sub> (0.060 g, 0.06 mmol). The resulting solution was immediately frozen inside a 40 mL shaker tube glass insert. The glass insert was transferred to a shaker tube, and its contents allowed to thaw under an ethylene atmosphere. The reaction mixture was agitated under 6.9 MPa C<sub>2</sub>H<sub>4</sub> for 18 h at ambient temperature. The final reaction mixture contained polyethylene, which was washed with methanol and dried; yield of polymer = 8.9 g. <sup>1</sup>H NMR (CDCl<sub>2</sub>CDCl<sub>2</sub>, 120°C) showed that this sample contained 47 methyl-ended branches per 1000 methylenes. DSC: T<sub>m</sub> = 112.1°C, ΔH<sub>f</sub> = 57.5 J/g.

#### Example 250

A 100 mL autoclave was charged with a solution of Pd<sub>2</sub>(dba)<sub>3</sub> (dba = dibenzylideneacetone) (0.054 g, 0.059 mmol) in 40 mL of chloroform. A solution of (2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>·HBAF·(Et<sub>2</sub>O)<sub>2</sub> (0.085 g, 0.059 mmol) (see Example 256) in 10 mL of chloroform was then added under 2.1 MPa of ethylene. The reaction mixture was stirred for 3 h. During this time the temperature inside the reactor varied between 24 and 40°C. Ethylene was then vented, and the product polymer was precipitated by addition of the crude reaction mixture to methanol. The polymer was dried affording 14.7 g of viscous polyethylene. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25°C) of this

material showed it to be branched polyethylene with 115 methyl-ended branches per 1000 methylenes. GPC analysis in trichlorobenzene gave  $M_n = 97,300$ ,  $M_w = 225,000$  vs. linear polyethylene.

5                                    Example 251

A 100 mL autoclave was charged with solid  $\text{Pd}(\text{OAc})_2$  (OAc = acetate) (0.027 g, 0.12 mmol) and (2,6-i-PrPh) $_2$ DABMe $_2$  (0.049 g, 0.12 mmol). The reactor was flushed with nitrogen and evacuated. A solution of 54  
10 wt. %  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  (0.098 g, 0.60 mmol) in 10 mL of chloroform was then added under 2.1 MPa of ethylene. The reaction mixture was stirred for 1.5 h. During this time, the temperature inside the reactor varied between 24 and 37°C. Ethylene was then vented, and the  
15 product polymer was precipitated by addition of the crude reaction mixture to methanol. The polymer was dried affording 4.00 g of viscous polyethylene.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 25°C) of this material showed it to be branched polyethylene with 100 methyl-ended branches per 1000  
20 methylenes. GPC analysis in trichlorobenzene gave  $M_n = 30,500$ ,  $M_w = 43,300$  vs. linear polyethylene.

Example 252

(Note: It is believed that in the following experiment, adventitious oxygen was present and acted  
25 as a cocatalyst.) Under nitrogen, [(2,6-i-PrPh) $_2$  DAB An]Ni(COD) (0.006 g, 0.009 mmol) and 9.6 wt. % MAO in toluene (0.54 mL, 1.66 mmol) were dissolved in 50 mL of toluene. This mixture was then transferred to a 100 mL autoclave. The autoclave was then charged with 2.1 MPa  
30 of ethylene. The reaction mixture was stirred for 8 min. During this time, the temperature inside the reactor varied between 23 and 51°C. Ethylene pressure was then vented. The product polymer was washed with methanol and dried, affording 8.44 g of polyethylene.  
35  $^1\text{H}$  NMR ( $\text{CDCl}_2$ , 120°C) showed that this sample contained 77 methyl-ended branches per 1000 methylenes.

Example 253

Under nitrogen, [(2,4,6-MePh)DABAn]NiBr<sub>2</sub> (0.041 g, 0.065 mmol) was suspended in cyclopentene (43.95 g, 645 mmol). To this was added a 1 M solution of EtAlCl<sub>2</sub> in toluene (3.2 mL, 3.2 mmol). The resulting reaction mixture was transferred to an autoclave, and under 700 kPa of nitrogen heated to 60°C. The reaction mixture was stirred at 60°C for 18 h; heating was then discontinued. When the reactor temperature had dropped to -30°C, the reaction was quenched by addition of isopropanol. The resulting mixture was stirred under nitrogen for several minutes. The mixture was then added under air to a 5 % aqueous HCl solution (200 mL). The precipitated product was filtered off, washed with acetone, and dried to afford 6.2 g of polycyclopentene as a white powder. DSC of this material showed a broad melting transition centered at approximately 190°C and ending at approximately 250°C;  $\Delta H_f = 18$  J/g. Thermal gravimetric analysis of this sample showed a weight loss starting at 184°C: the sample lost 25% of its weight between 184 and 470°C, and the remaining material decomposed between 470 and 500°C.

#### Example 254

Under nitrogen, [(2,6-Me-4-BrPh)<sub>2</sub>DABMe<sub>2</sub>]NiBr<sub>2</sub> (0.010 g, 0.015 mmol) was suspended in cyclopentene (5.0 g, 73.4 mmol). To this was added a 1 M solution of EtAlCl<sub>2</sub> in toluene (0.75 mL, 0.75 mmol). The resulting reaction mixture was stirred at room temperature for 92 h, during which time polycyclopentene precipitated. The reaction was then quenched by addition of -5 mL of methanol under nitrogen. Several drops of concentrated HCl was then added under air. The product was then filtered off, washed with more methanol followed by acetone, and dried to afford 1.31 g of polycyclopentene as a white powder. DSC of this material showed a broad melting transition centered at approximately 200°C and ending at approximately 250°C;  $\Delta H_f = 49$  J/g. Thermal gravimetric analysis of this sample showed a weight

loss starting at  $-477^{\circ}\text{C}$ ; the sample completely decomposed between  $477$  and  $507^{\circ}\text{C}$ .

Example 255

Under nitrogen,  $[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{NiBr}_2$  ( $0.008$  g,  $0.015$  mmol) was suspended in cyclopentene ( $5.00$  g,  $73.4$  mmol). To this was added a  $1$  M solution of  $\text{EtAlCl}_2$  in toluene ( $0.75$  mL,  $0.75$  mmol). A magnetic stirbar was added to the reaction mixture and it was stirred at room temperature; after  $92$  h at room temperature the reaction mixture could no longer be stirred due to precipitation of polycyclopentene solids. At this point the reaction was then quenched by addition of  $\sim 5$  mL of methanol under nitrogen. Several drops of concentrated  $\text{HCl}$  was then added under air. The product was then filtered off, washed with more methanol followed by acetone, and dried to afford  $2.75$  g of polycyclopentene as a white powder. DSC of this material showed a broad melting transition centered at approximately  $190^{\circ}\text{C}$  and ending at approximately  $250^{\circ}\text{C}$ ;  $\Delta H_f = 34$  J/g. Thermal gravimetric analysis of this sample showed a weight loss starting at  $-480^{\circ}\text{C}$ ; the sample completely decomposed between  $480$  and  $508^{\circ}\text{C}$ .

Example 256

$\text{HBAF}$  ( $0.776$  mmol) was dissolved in  $5$  ml of  $\text{Et}_2\text{O}$ . A second solution of  $0.776$  mmol of  $(2,6\text{-i-PrPh})_2\text{DABMe}_2$  in  $3$  ml of  $\text{Et}_2\text{O}$  was added. The reaction turned deep red-brown immediately. After stirring for  $2$  h the volatiles were removed in vacuo to give the protonated  $\alpha$ -diimine salt which was a red crystalline solid.

Example 257

$\text{HBF}_4$  ( $0.5$  mmol) was dissolved in  $4$  ml of  $\text{Et}_2\text{O}$ . A second solution of  $0.5$  mmol of  $(2,6\text{-i-PrPh})_2\text{DABMe}_2$  in  $3$  ml of  $\text{Et}_2\text{O}$  was added. A color change to deep red occurred upon mixing. The reaction was stirred overnight. The volatiles were removed in vacuo to give the protonated  $\alpha$ -diimine salt which was an orange solid.



Example 258

HO<sub>3</sub>SCF<sub>3</sub> (0.5 mmol) was dissolved in 4 ml of Et<sub>2</sub>O. A second solution of 0.5 mmol of (2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub> in 3 ml of Et<sub>2</sub>O was added. A color change to deep red occurred upon mixing after a few minutes a yellow-orange precipitate began to form. The reaction was stirred overnight. The product, believed to be the protonated α-diimine salt, was isolated by filtration rinsed with Et<sub>2</sub>O and dried in vacuo.

10

Example 259

HBAF (0.478 mmol) was dissolved in 5 ml of Et<sub>2</sub>O. A second solution of 0.776 mmol of [(2,6-i-PrPh)N=C(CH<sub>3</sub>)]<sub>2</sub>CH<sub>2</sub> in 3 ml of Et<sub>2</sub>O was added. The reaction was stirred overnight. Removal of the volatiles in vacuo gave an off white solid, believed to be the protonated 1,3-diimine salt.

15

Example 260

HBF<sub>4</sub> (0.478 mmol) was dissolved in 5 ml of Et<sub>2</sub>O. A second solution of 0.478 mmol of [(2,6-i-PrPh)N=C(CH<sub>3</sub>)]<sub>2</sub>CH<sub>2</sub> in 3 ml of Et<sub>2</sub>O was added, the reaction turned cloudy with a white precipitate. The reaction was stirred overnight. The white solid, believed to be the protonated 1,3-diimine salt, was isolated by filtration rinsed with Et<sub>2</sub>O and dried in vacuo.

20

25

Example 261

The product of Example 256 (78 mg) was dissolved in 20 ml of toluene. The reaction vessel was charged with 140 kPa (absolute) of ethylene. A solution of 10 mg Ni(COD)<sub>2</sub> in 3 ml of toluene was added. Ethylene was added (138 kPa pressure, absolute) and the polymerization was run for 24 h at ambient temperature. Precipitation with MeOH gave 157 mg of white spongy polyethylene.

30

Example 262

The product of Example 257 (27 mg) was dissolved in 20 ml of toluene. The reaction vessel was charged with 35 kPa of ethylene. A solution of 10 mg Ni(COD)<sub>2</sub> in 3 ml of toluene was added. Ethylene was added (138 kPa pressure, absolute) and the polymerization was run for 24 h at ambient temperature. Precipitation with MeOH gave 378 mg of sticky white polyethylene.

Example 263

The product of Example 258 (30 mg) was dissolved in 20 ml of toluene. The reaction vessel was charged with 140 kPa (absolute) of ethylene. A solution of 10 mg Ni(COD)<sub>2</sub> in 3 ml of toluene was added. Ethylene was added (138 kPa pressure, absolute) and the polymerization was run for 24 h at ambient temperature. Precipitation with MeOH gave 950 mg of amorphous polyethylene.

Example 264

To a burgundy slurry of 1 mmol of VCl<sub>3</sub>·(THF)<sub>3</sub> in 10 ml of THF was added a yellow solution of 1 mmol of (2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub> in 4 ml of THF. After 10 minutes of stirring the reaction was a homogenous red solution. The solution was filtered to remove a few solids, concentrated and then cooled to -30°C. The red crystals that formed were isolated by filtration, rinsed with pentane and dried in vacuo. The yield was 185 mg.

Example 265

The product of Example 264 (6 mg) was dissolved in 20 ml of toluene. The resulting solution was placed under 140 kPa (absolute) of ethylene. PMAO solution (0.8 mL, 9.6 wt% Al in toluene) was added and the polymerization was stirred for 3 h. The reaction was halted by the addition of 10% HCl/MeOH. The precipitated polymer was isolated by filtration, washed with MeOH and dried in vacuo. The yield was 1.58 g of white polyethylene.

Example 266

Lanthanide metal tris-triflates (wherein the lanthanide metals were Y, La, Sm, Er, and Yb), 1 mmol, was slurried in 10 ml of CH<sub>2</sub>Cl<sub>2</sub>. A solution of 1 mmol of (2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub> in 3 ml of CH<sub>2</sub>Cl<sub>2</sub> was added and the reaction stirred for 16 h at ambient temperature. The solution was filtered to give a clear filtrate. Removal of the solvent in vacuo gave light yellow to orange powders.

Example 267

Each of the various materials (0.02 mmol) prepared in Example 266 were dissolved in 20 ml of toluene. The resulting solutions were placed under 140 kPa (absolute) of ethylene. MMAO-3A solution (1.0 mL, 6.4 wt% Al in toluene) was added and the polymerizations were stirred for 3 h. The reactions were halted by the addition of 10% HCl/MeOH. The precipitated polymers were isolated by filtration washed with MeOH and dried in vacuo. Polymer yields are shown the following table,

	<u>Lanthanide Metal</u>	<u>Yield (g)</u>
	Yb	0.117
	La	0.139
	Sm	0.137
25	Y	0.139
	Er	0.167

Example 268

[(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>]Ni-02 (68 mg) was dissolved in 20 ml of toluene. The reaction vessel was placed under 138 kPa (absolute) of ethylene. PMAO (0.7 mL, 9.6 wt.% Al in toluene) was added and the polymerization was conducted for 16 h. The reaction was halted by the addition of 15 ml of 10% HCl/MeOH solution. The precipitated polymer was isolated by filtration and dried under vacuum to yield 1.67 g of rubbery polyethylene.

Example 269

[(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>]Ni-0<sub>2</sub> (65 mg) was dissolved in 20 ml of toluene. The reaction vessel was placed under 138 kPa (absolute) of ethylene. PMAO (0.7 mL, 9.6 wt.% Al in toluene) was added and the polymerization was conducted for 16 h. The reaction was halted by the addition of 15 ml of 10% HCl/MeOH solution. The precipitated polymer was isolated by filtration and dried under vacuum to yield 1.9 g of rubbery polyethylene.

Example 270

[(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>]CrCl<sub>2</sub>·(THF) (15 mg) was dissolved in 20 ml of toluene. The reaction vessel was placed under 138 kPa (absolute) of ethylene. MMAO-3A (1 mL, 6.4 wt.% Al in toluene) was added and the polymerization was conducted for 3 h. The reaction was halted by the addition of 15 ml of 10% HCl/MeOH solution. The precipitated polymer was isolated by filtration and dried under vacuum to yield 694 mg of polyethylene. DSC (-150 to 250°C at 10°C/min) results from the second heating were T<sub>m</sub> 129°C, ΔH<sub>f</sub> 204 J/g.

Example 271

[(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>]CrCl<sub>3</sub> (14 mg) was dissolved in 20 ml of toluene. The reaction vessel was placed under 138 kPa (absolute) of ethylene. MMAO-3A (1 mL, 6.4 wt.% Al in toluene) was added and the polymerization was conducted for 3 h. The reaction was halted by the addition of 15 ml of 10% HCl/MeOH solution. The precipitated polymer was isolated by filtration and dried under vacuum to yield 833 mg of polyethylene. DSC (-150 to 250°C at 10°C/min) results from the second heating were T<sub>m</sub> 133°C, ΔH<sub>f</sub> 211 J/g.

Example 272

[(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>]CrCl<sub>2</sub>·(THF) (14 mg) was dissolved in 20 ml of toluene. The reaction vessel was placed under 138 kPa (absolute) of ethylene. MMAO-3A (1 mL, 6.4 wt.% Al in toluene) was added and the polymerization was conducted for 3 h. The reaction was

halted by the addition of 15 ml of 10% HCl/MeOH solution. The precipitated polymer was isolated by filtration and dried under vacuum to yield 316 mg of polyethylene. DSC results from the second heating were  
5 (-150 to 250°C at 10°C/min)  $T_m$  133°C,  $\Delta H_f$  107 J/g.

Example 273

[(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>]CrCl<sub>3</sub> (15 mg) was dissolved in 20 ml of toluene. The reaction vessel was placed under 138 kPa (absolute) of ethylene. MMAO-3A (1 mL,  
10 6.4 wt.% Al in toluene) was added and the polymerization was conducted for 3 h. The reaction was halted by the addition of 15 ml of 10% HCl/MeOH solution. The precipitated polymer was isolated by filtration and dried under vacuum to yield 605 mg of  
15 polyethylene. DSC (-150 to 250°C at 10°C/min) results from the second heating were  $T_m$  134°C,  $\Delta H_f$  157 J/g.

Example 274

A 61 mg sample of {[(2,6-i-PrPh)<sub>2</sub>DABAn]Ni( $\eta^3$ -H<sub>2</sub>CCHCHCl))BAF was dissolved in 20 ml of toluene. The  
20 reaction vessel was placed under 138 kPa (absolute) of ethylene. PMAO (0.7 mL) was added and the reaction stirred for 16 h. The polymerization was quenched by the addition of 15 ml of 10% HCl/MeOH. The polymer was isolated by filtration, washed with acetone and dried.  
25 The yield was 2.24 g of rubbery polyethylene.

Example 275

A 65 mg sample of {[(2,4,6-MePh)<sub>2</sub>DABAn]Ni( $\eta^3$ -H<sub>2</sub>CCHCHCl))BAF was dissolved in 20 ml of toluene. The  
30 reaction vessel was placed under 138 kPa (absolute) of ethylene. PMAO (0.7 mL) was added and the reaction stirred for 16 h. The polymerization was quenched by the addition of 15 ml of 10% HCl/MeOH. The polymer was isolated by filtration, washed with acetone and dried.  
The yield was 2.0 g of rubbery polyethylene.

35

Example 276

A 61 mg sample of {[(2,6-iPrPh)<sub>2</sub>DABAn]Ni( $\eta^3$ -H<sub>2</sub>CCHCH<sub>2</sub>))Cl was dissolved in 20 ml of toluene. The reaction vessel was placed under 138 kPa (absolute) of

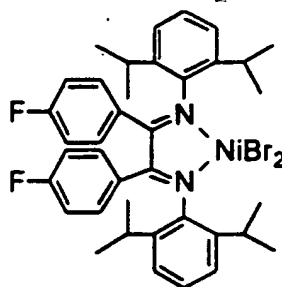
ethylene. PMAO (0.7 mL) was added and the reaction stirred for 16 h. The polymerization was quenched by the addition of 15 ml of 10% HCl/MeOH. The polymer was isolated by filtration, washed with acetone and dried.  
 5 The yield was 1.83 g of rubbery polyethylene.

#### Example 277

A 60 mg sample of  $\{[(2,6\text{-iPrPh})_2\text{DABMe}_2]\text{Ni}(\eta^3\text{-H}_2\text{CCHCH}_2)\}\text{Cl}$  was dissolved in 20 ml of toluene. The reaction vessel was placed under 138 kPa (absolute) of  
 10 ethylene. PMAO (0.7 mL) was added and the reaction stirred for 16 h. The polymerization was quenched by the addition of 15 ml of 10% HCl/MeOH. The polymer was isolated by filtration, washed with acetone and dried. The yield was 1.14 g of rubbery polyethylene.

15

#### Example 278



In a 250-mL RB flask fitted with pressure  
 20 equalizing addition funnel, thermometer, magnetic stirrer, and N<sub>2</sub> inlet was placed 0.75g (3.0mmol) of 4,4'-difluorobenzil, 13.8mL (80mmol) of 2,6-diisopropylaniline (DIPA), and 100mL dry benzene. In the addition funnel was placed 50mL of dry benzene and  
 25 2.0mL (3.5g; 18mmol) of titanium tetrachloride. The reaction flask was cooled to 2°C with ice and the TiCl<sub>4</sub> solution was added dropwise over 45min, keeping the reaction temperature below 5°C. The ice bath was removed after addition was complete and the mixture was  
 30 stirred at RT for 72h. The reaction mixture was partitioned between water and ethyl ether, and the ether phase was rotovapped and the concentrated oil was

washed with 800mL 1N HCl to remove the excess diisopropylaniline. The mixture was extracted with 100mL of ether, and the ether layer was washed with water and rotovapped. Addition of 15mL hexane plus 5 30mL of methanol to the concentrate resulted in the formation of fine yellow crystals which were filtered, methanol-washed, and dried under suction to yield 0.4g of (2,6-i-PrPh)<sub>2</sub>DAB(4-F-Ph)<sub>2</sub>, mp: 155-158°C.

A 60-mg (0.092-mmol) sample of (2,6-i-PrPh)<sub>2</sub>DAB(4-F-Ph)<sub>2</sub> 10 was stirred under nitrogen with 32mg (0.103mmol) of nickel(II) dibromide-dimethoxyethane complex in 20mL of methylene chloride for 66h. The orange-brown solution was rotovapped and held under high vacuum for 2h to yield 86mg of red-brown solids. 15 The solid product was scraped from the sides of the flask, stirred with 20mL hexane, and allowed to settle. The yellow-orange hexane solution was pipetted off and the remaining solid was held under high vacuum to yield 48mg of the orange-brown complex [(2,6-i-PrPh)<sub>2</sub>DAB(4-F-Ph)<sub>2</sub>]NiBr<sub>2</sub>. 20

#### Example 279

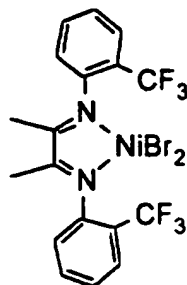
Ethylene polymerization with [(2,6-i-PrPh)<sub>2</sub>DAB(4-F-Ph)<sub>2</sub>]NiBr<sub>2</sub>

A 26-mg (0.033-mmol) sample of [(2,6-i-PrPh)<sub>2</sub>DAB(4-F-Ph)<sub>2</sub>]NiBr<sub>2</sub> 25 was magnetically stirred under nitrogen in a 50-mL Schlenk flask with 25mL of dry toluene. Then 0.6mL of polymethylalumoxane was injected, turning the orange-brown solution to a deep green- black solution. The mixture was pressurized 30 immediately with ethylene to 152 kPa (absolute) and stirred at RT for 17h. The reaction soon became warm to the touch; this heat evolution persisted for over an hour and the liquid volume in the Schlenk flask was observed to be slowly increasing. After 17h, the 35 reaction was still dark green-brown, but thicker and significantly (20%) increased in volume. The ethylene was vented; the offgas contained about 3% butenes (1-butene, 1.9%; t-2-butene, 0.6%; c-2-butene, 0.9%) by GC

(30-m Quadrex GSQ Megabore column; 50-250°C at 10°/min). The toluene solution was stirred with 6N HCl/methanol and was separated; the toluene was rotovapped and held under high vacuum to yield 9.53g of low-melting polyethylene wax. There seemed to be significant low-boiling species present, probably low-mw ethylene oligomers, which continued to boil off under high vacuum. <sup>1</sup>H NMR (CDCl<sub>3</sub>; 60°C) of the product showed a CH<sub>2</sub>:CH<sub>3</sub> ratio of 206:17, which is 57 CH<sub>3</sub>'s per 1000 CH<sub>2</sub>'s. There were vinyl peaks at 5-5.8ppm; if the end groups are considered to be vinyls rather than internal olefins, the degree of polymerization was about 34.

Example 280

15            Synthesis of [(2-CF<sub>3</sub>Ph)<sub>2</sub>DABMe<sub>2</sub>]NiBr<sub>2</sub>



[(2-CF<sub>3</sub>Ph)<sub>2</sub>DABMe<sub>2</sub>]NiBr<sub>2</sub>

A mixture of 10.2mL (13.1g; 81.2mmol) 2-aminobenzotrifluoride and 3.6mL (3.5g; 41mmol) freshly-distilled 2,3-butanedione in 15mL methanol containing 6 drops of 98% formic acid was stirred at 35°C under nitrogen for 8 days. The reaction mixture was rotovapped and the resultant crystalline solids (1.3g) were washed with carbon tetrachloride. The crystals were dissolved in chloroform; the solution was passed through a short alumina column and evaporated to yield 1.0g of yellow crystals of the diimine (2-CF<sub>3</sub>Ph)<sub>2</sub>DABMe<sub>2</sub>. <sup>1</sup>H NMR analysis (CDCl<sub>3</sub>): 2.12ppm (s, 6H, CH<sub>3</sub>); 6.77 (d, 2H, ArH, J=9Hz); 7.20 (t, 2H, ArH, J=7Hz); 7.53 (t, 2H, ArH, J=7Hz); 7.68 (t, 2H, ArH,



J=8Hz). Infrared spectrum: 1706, 1651, 1603, 1579, 1319, 1110cm<sup>-1</sup>. Mp: 154-156°C.

A mixture of 0.207g (0.56mmol) of (2-CF<sub>3</sub>Ph)<sub>2</sub>DABMe<sub>2</sub> and 0.202g (0.65mmol) of nickel(II) dibromide-dimethoxyethane complex in 13mL of methylene chloride was stirred at RT under nitrogen for 3hr. The red-brown suspension was rotovapped and held under high vacuum to yield 0.3g of [(2-CF<sub>3</sub>Ph)<sub>2</sub>DABMe<sub>2</sub>]NiBr<sub>2</sub> complex.

Example 281

10 Ethylene polymerization with[(2-CF<sub>3</sub>Ph)<sub>2</sub>DABMe<sub>2</sub>]NiBr<sub>2</sub>  
A 13-mg (0.022-mmol) sample of [(2-CF<sub>3</sub>Ph)<sub>2</sub>DABMe<sub>2</sub>]NiBr<sub>2</sub> was placed in a Parr® 600-mL stirred autoclave; 200mL of dry, deaerated hexane (dried over molecular sieves) was added and the hexane  
15 was saturated with ethylene by pressurizing to 450 kPa (absolute) ethylene and venting. Then 1.0mL of modified methylalumoxane (1.7M in heptane; contains about 30% isobutyl groups) was injected into the autoclave with stirring, and the autoclave was stirred  
20 for 1hr under 690 kPa (absolute) ethylene as the temperature rose from 20°C to 61°C over the first 20min and then slowly declined to 48°C by the end of the run. The ethylene was vented and 3mL of methanol was injected to stop polymerization; the autoclave  
25 contained a white suspension of fine particles of polyethylene; the appearance was like latex paint. The polymer suspension was added to methanol, and the polymer was stirred with MeOH/HCl to remove catalyst. The suspension was filtered and dried in a vacuum oven  
30 (75°C) to yield 26.8g of fine, white powdery polyethylene. Differential scanning calorimetry (15°C/min): Tg -45°C; mp 117°C (75J/g). GPC (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal  
35 calibration theory): Mn=2,350; Mw=8,640; Mz=24,400; Mw/Mn=3.67. A solution of the polymer in chlorobenzene could be cast into a waxy film with little strength.

Example 282

Under nitrogen,  $\text{Ni(COD)}_2$  (0.017 g, 0.062 mmol) and (2,4,6-MePh)<sub>2</sub>DABAn (0.026 g, 0.062 mmol) were dissolved in 2.00 g of cyclopentene to give a purple solution.

5 The solution was then exposed to air (oxygen) for several seconds. The resulting dark red-brown solution was then put back under nitrogen, and  $\text{EtAlCl}_2$  (1 M solution in toluene, 3.0 mL, 3.0 mmol) added. A cranberry-red solution formed instantly. The reaction

10 mixture was stirred at room temperature for 3 days, during which time polycyclopentene precipitated. The reaction was then quenched by the addition of methanol followed by several drops of concentrated HCl. The reaction mixture was filtered, and the product polymer

15 washed with methanol and dried to afford 0.92 g of polycyclopentene as an off-white powder. Thermal gravimetric analysis of this sample showed a weight loss starting at 141°C: the sample lost 18% of its weight between 141 and 470°C, and the remaining

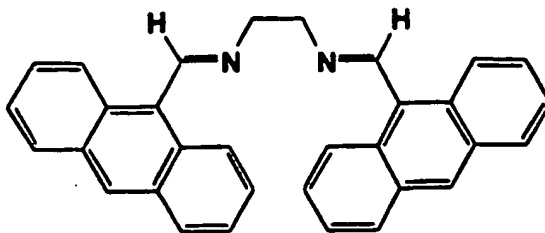
20 material decomposed between 470 and 496°C.

Example 283

Under a nitrogen atmosphere,  $\text{Ni(COD)}_2$  (0.017 g, 0.06 mmol) and the ligand shown below (0.025 g, 0.06 mmol) were dissolved in benzene (5.0 mL). To the

25 resulting solution was added  $\text{HBAF}^+(\text{Et}_2\text{O})_2$  (0.060 g, 0.06 mmol). The resulting solution was immediately frozen inside a 40 mL shaker tube glass insert. The glass insert was transferred to a shaker tube, and its contents allowed to thaw under an ethylene atmosphere.

30 The reaction mixture was agitated under 6.9 MPa  $\text{C}_2\text{H}_4$  for 18 h at ambient temperature. The final reaction mixture contained polyethylene, which was washed with methanol and dried; yield of polymer = 11.0 g.

Example 284

The catalyst  $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdCH}_2\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OCH}_3\}^+\text{SbF}_6^-$  (0.025g, 0.03 mmol) and  $\text{CH}_2=\text{CH}(\text{CH}_2)_6\text{C}_{10}\text{F}_{21}$  (4.74g, 7.52 mmol) were dissolved in 20 mL  $\text{CH}_2\text{Cl}_2$  in a Schlenk flask in a drybox. The flask was connected to a Schlenk line and the flask was then briefly evacuated and refilled with ethylene from the Schlenk line. This was stirred at RT under 1 atm of ethylene for 72 hr. Solvent was evaporated to almost dryness. Acetone (70 mL) was added and the mixture was stirred vigorously overnight. The upper layer was decanted. The resulting yellow solid was washed with 3x15 mL acetone, vacuum dried, and 1.15g of product was obtained.  $^1\text{H}$  NMR analysis ( $\text{CD}_2\text{Cl}_2$ ): 105 methylys per 1000 methylene carbons. Comparison of the integral of the  $\text{CH}_2\text{R}_f$  (2.10 ppm) with the integrals of methylys (0.8-1.0 ppm) and methylenes (1.2-1.4 ppm) indicated a comonomer content of 6.9 mol%. The polymer exhibited a glass transition temperature of  $-55^\circ\text{C}$  (13J/g) and a melting point of  $57^\circ\text{C}$  by differential scanning calorimetry. Gel permeation chromatography (THF, polystyrene standard):  $M_w = 39,500$ ,  $M_n = 34,400$ ,  $P/D = 1.15$ .

Example 285

In a 100 mL Schlenk flask,  $[(2,6\text{-i-PrPh})_2\text{DABAn}]\text{NiBr}_2$  (0.012g, 0.017mmol) and  $\text{CH}_2=\text{CH}(\text{CH}_2)_6\text{C}_{10}\text{F}_{21}$  (4.62g, 7.33 mmol) were dissolved in 32 mL of toluene under stirring. This was pressured with 1 atm ethylene and was allowed to stir at  $0^\circ\text{C}$  for 15 minutes. MAO (1.7 mL, 8.9 wt% in toluene) was added. This was allowed to vigorously stir at RT for

30 min. Sixty mL methanol was then added. The white solid was filtered, followed by 3x30 ml 3:1 methanol/toluene wash, vacuum dried, and 3.24g of white polymer was obtained. <sup>1</sup>H NMR analysis (o-dichlorobenzene-d<sub>4</sub>, 135 °C): 64 methylys per 1000 methylene carbons. Comparison of the integral of the CH<sub>2</sub>R<sub>f</sub> (2.37ppm) with the integrals of methylys (1.1-1.2 ppm) and methylenes (1.4-1.8 ppm) indicated a comonomer content of 8.7 mol%. Mw = 281,157, Mn = 68,525, P/D = 4.1.

#### Example 286

In a 100 mL Schlenk flask, [(2,6-i-PrPh)<sub>2</sub>DABAn]NiBr<sub>2</sub> (0.012g, 0.017mmol) and CH<sub>2</sub>=CH(CH<sub>2</sub>)<sub>6</sub>C<sub>10</sub>F<sub>21</sub> (4.62g, 7.33 mmol) were dissolved in 32 mL of toluene under stirring. This was allowed to stir at 0 °C for 15 minutes. MAO (1.7 mL, 8.9 wt% in toluene) was added. This was allowed to stir at 0°C for 2.5 h and then RT for 3 h. Methanol (200 mL) was then added, followed by 1 mL conc. HCl. The white solid was filtered and washed with methanol, vacuum dried, and 0.79g of white solid polymer was obtained. By differential scanning calorimetry, Tm 85°C(22J/g).

#### Example 287

{[(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>]PdCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C(O)OCH<sub>3</sub>}<sup>+</sup>SbF<sub>6</sub><sup>-</sup> (0.0205g, 0.024 mmol) and CH<sub>2</sub>=CH(CH<sub>2</sub>)<sub>4</sub>(CF<sub>2</sub>)<sub>4</sub>O(CF<sub>2</sub>)<sub>2</sub>SO<sub>2</sub>F (3.5g, 7.26 mmol) were dissolved in 18 mL CH<sub>2</sub>Cl<sub>2</sub> in a Schlenk flask in a drybox. The flask was connected to a Schlenk line and the flask was then briefly evacuated and refilled with ethylene from the Schlenk line. This was stirred at RT under 1 atm of ethylene for 72 hr. Solvent was evaporated after filtration. The viscous oil was dissolved in 10 mL CH<sub>2</sub>Cl<sub>2</sub>, followed by addition of 100 mL methanol. The upper layer was decanted. The reverse precipitation was repeated two more time, followed by vacuum drying to yield 3.68g of a light yellow viscous oil. <sup>1</sup>H NMR analysis (CDCl<sub>3</sub>): 89 methylys per 1000 methylene carbons. Comparison of the integral of the CH<sub>2</sub>CF<sub>2</sub>- (2.02 ppm) with the integrals

of methyls (0.8-1.0 ppm) and methylenes (1.1-1.4 ppm) indicated a comonomer content of 8.5 mol%.  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ): 45.27 ppm,  $-\text{SO}_2\text{F}$ ; -82.56 ppm, -83.66 ppm, -112.82 ppm, -115.34 ppm, -124.45 ppm, -125.85 ppm,  $\text{CF}_2$  peaks. The polymer exhibited a glass transition temperature of  $-57^\circ\text{C}$  by differential scanning calorimetry. Gel permeation chromatography (THF, polystyrene standard):  $M_w = 120,000$ ,  $M_n = 78,900$ ,  $P/D = 1.54$ . The turnover numbers for ethylene and the comonomer are 2098 and 195, respectively.

#### Example 288

In a 100 mL Schlenk flask,  $[(2,6\text{-i-PrPh})_2\text{DABAN}]\text{NiBr}_2$  (0.017g, 0.024 mmol) and  $\text{CH}_2=\text{CH}(\text{CH}_2)_4(\text{CF}_2)_4\text{O}(\text{CF}_2)_2\text{SO}_2\text{F}$  (5.0g, 10 mmol) were dissolved in 25 mL of toluene under stirring. MAO (2.3 mL, 8.9 wt% in toluene) was added. This was allowed to stir at RT for 15 hr. Sixty mL methanol was then added, followed by 1 mL conc. HCl. The upper layer was decanted, residue washed with methanol (5x5 mL), vacuum dried, and 1.20g of a white viscous oil was obtained.  $^{19}\text{F}$  NMR (Hexafluorobenzene,  $80^\circ\text{C}$ ): 45.20 ppm,  $-\text{SO}_2\text{F}$ ; -81.99 ppm, -82.97 ppm, -112.00 ppm, -114.36 ppm, -123.60 ppm, -124.88 ppm,  $\text{CF}_2$  peaks.

#### Example 289

In a Schlenk flask,  $[(2,6\text{-i-PrPh})_2\text{DABAN}]\text{NiBr}_2$  (0.012g, 0.017mmol) and  $\text{CH}_2=\text{CH}(\text{CH}_2)_4(\text{CF}_2)_4\text{O}(\text{CF}_2)_2\text{SO}_2\text{F}$  (3.26g, 6.77mmol) were dissolved in 35 mL of toluene under stirring. This was pressured with 1 atm ethylene and was allowed to stir at  $0^\circ\text{C}$  for 15 minutes. MAO (1.7 mL, 8.9 wt% in toluene) was added. This was allowed to vigorously stir at RT for 45 minutes. Methanol (140 mL) was then added, followed by addition of 1 mL of conc. HCl. The white solid was filtered, followed by methanol wash, vacuum dried to obtain 2.76g of a white rubbery polymer.  $^1\text{H}$  NMR analysis (o-dichlorobenzene- $d_4$ ,  $100^\circ\text{C}$ ): 98 methyls per 1000 methylene carbons. Comparison of the integral of the  $\text{CH}_2\text{CF}_2$ - (2.02 ppm) with the integrals of methyls (0.8-

1.0 ppm) and methylenes (1.1-1.4 ppm) indicated a comonomer content of 3.5 mol%.  $^{19}\text{F}$  NMR ((0-dichlorobenzene- $d_4$ ): 45.19 ppm,  $-\text{SO}_2\text{F}$ ; -82.70 ppm, -83.72 ppm, -112.96 ppm, -115.09 ppm, -124.37 ppm, -125.83 ppm,  $\text{CF}_2$  peaks. The polymer exhibited  $T_m$  of  $97^\circ\text{C}$  by differential scanning calorimetry.  $M_w = 156,000$ ,  $M_n = 90,000$ ,  $P/D = 1.73$ .

#### Example 290

{[(2,6-*i*-PrPh) $_2$ DABMe $_2$ ]PdCH $_2$ CH $_2$ CH $_2$ C(O)OCH $_3$ } $^+$ SbF $_6^-$  (0.030g, 0.035 mmol) and CH $_2$ =CH(CH $_2$ ) $_4$ (CF $_2$ ) $_2$ CO $_2$ Et (3.0g, 11.7 mmol) were dissolved in 20 mL CH $_2$ Cl $_2$  in a Schlenk flask in a drybox. The flask was connected to a Schlenk line and the flask was then briefly evacuated and refilled with ethylene from the Schlenk line. This was stirred at RT under 1 atm of ethylene for 72 h. Solvent was evaporated. The viscous oil was dissolved in 10 mL acetone, followed by addition of 60 mL methanol. The mixture was centrifuged. The upper layer was decanted. The oil was dissolved in 10 mL acetone followed by addition of 60 mL methanol. The mixture was centrifuged again. The viscous oil was collected, and vacuum dried to obtain 1.50g of a light yellow viscous oil.  $^1\text{H}$  NMR analysis (CDCl $_3$ ): 67 methyls per 1000 methylene carbons. Comparison of the integral of the CH $_2$ CF $_2$ - (2.02 ppm) with the integrals of methyls (0.8-1.0 ppm) and methylenes (1.1-1.4 ppm) indicated a comonomer content of 11 mol%. The polymer exhibited a  $T_g$  of  $-61^\circ\text{C}$  by DSC. GPC (THF, polystyrene standard):  $M_w = 73,800$ ,  $M_n = 50,500$ ,  $P/D = 1.46$ .

#### Example 291

In a Schlenk flask, [(2,6-*i*-PrPh) $_2$ DABAn]NiBr $_2$  (0.019g, 0.026 mmol) and CH $_2$ =CH(CH $_2$ ) $_4$ (CF $_2$ ) $_2$ CO $_2$ Et (3.0g, 11.7 mmol) were dissolved in 35 mL of toluene. This was placed under 1 atm of ethylene at  $0^\circ\text{C}$  for 15 minutes. MAO (2.6 mL, 8.9 wt% in toluene) was added. This was allowed to vigorously stir at  $0^\circ\text{C}$  for 30 minutes. Methanol (120 mL) was then added, followed by 1 mL conc. HCl. The solid was filtered, washed with

methanol and hexane, and vacuum dried to yield 1.21g of a white rubbery solid.  $^1\text{H}$  NMR analysis ( $\text{TCE-d}_2$ ,  $110^\circ\text{C}$ ): Comparison of the integral of the  $\text{CH}_2\text{CF}_2$ - (2.06 ppm) with the integrals of methyls (0.8-1.0 ppm) and methylenes (1.1-1.4 ppm) indicated a comonomer content of 6.0 mol%. The polymer exhibited a Tg of  $-46^\circ\text{C}$  and Tm's at  $40^\circ\text{C}$  and  $82^\circ\text{C}$  by DSC.

#### Example 292

In a Schlenk flask,  $[(2,6\text{-i-PrPh})_2\text{DABAn}]\text{NiBr}_2$  (0.022g, 0.030 mmol) and  $\text{CH}_2=\text{CH}(\text{CH}_2)_4(\text{CF}_2)_2\text{CO}_2\text{Et}$  (3.5g, 13.7 mmol) were dissolved in 30 mL of toluene. This was placed under nitrogen at  $0^\circ\text{C}$  for 15 minutes. MAO (3.0 mL, 8.9 wt% in toluene) was added. This was allowed to stir at  $0^\circ\text{C}$  for 2.5 h and then RT for 6 h. Fifty mL methanol was then added, followed by 1 mL conc. HCl. The mixture was washed with 3x60 mL water. The organic layer was isolated and dried by using  $\text{Na}_2\text{SO}_4$ . Evaporation of toluene and addition of hexane resulted in precipitation of an oil. The oil was washed with hexane another two times, and vacuum dried to yield 0.16g of a yellow oil.  $\text{MW} = 35,600$ ,  $\text{Mn} = 14,400$ ,  $\text{P/D} = 2.47$ .

#### Example 293

$\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdCH}_2\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OCH}_3\}^+\text{SbF}_6^-$  (0.0848g, 0.1 mmol) and  $\text{CH}_2=\text{CH}(\text{CH}_2)_4(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{SO}_2\text{F}$  (11.5g, 0.03 mol) were dissolved in 72 mL  $\text{CH}_2\text{Cl}_2$  in a Schlenk flask in a drybox. The flask was connected to a Schlenk line and the flask was then briefly evacuated and refilled with ethylene from the Schlenk line. This was stirred at RT under 1 atm of ethylene for 72 hr. The solution was filtered through Celite and then concentrated to 70 mL. Methanol (400 mL) was added under stirring. The upper layer was decanted. The oil was redissolved in 70 mL  $\text{CH}_2\text{Cl}_2$  followed by addition of 350 mL methanol. The viscous oil was collected, vacuum dried and 24.1g of a light yellow viscous oil was obtained.  $^1\text{H}$  NMR analysis ( $\text{CDCl}_3$ ): 113 methyls per 1000 methylene carbons. Comparison of the integral of

the  $\text{CH}_2\text{CF}_2$ - (2.0 ppm) with the integrals of  
 methyls (0.8-1.0 ppm) and methylenes (1.1-1.4 ppm)  
 indicated a comonomer content of 2.9 mol%. The polymer  
 exhibited a  $T_g$  of  $-66^\circ\text{C}$  by DSC. GPC (THF, polystyrene  
 5 standard):  $M_w = 186,000$ ,  $M_n = 90,500$ ,  $P/D = 2.06$ .  
 The turnover numbers for ethylene and the comonomer are  
 6,122 and 183, respectively.

#### Examples 294-300

All of these Examples were done under 1 atm  
 10 ethylene with a MA concentration of 1.2M and  
 $\{[(\text{diimine})\text{PdMe}(\text{Et}_2\text{O})]^+\text{SbF}_6^-\}$  concentration of 0.0022M  
 at RT for 72 hr. Results are shown in the Table below.

Ex. No.	Diimine	MA (mol%)*	Mn	P/D
294	(2,6-i- PrPh) <sub>2</sub> DABMe <sub>2</sub>	6	12,300	1.8
295	(2,6-EtPh) <sub>2</sub> DABMe <sub>2</sub>	16	7,430	1.9
296	(2,4,6- MePh) <sub>2</sub> DABMe <sub>2</sub>	23	2,840	2.1
297	(2,4,6-MePh) <sub>2</sub> DABAn	37	1,390	1.4
298	(2,4,6-MePh) <sub>2</sub> DABH <sub>2</sub>	46	1,090	3.1
299	(2-i-PrPh) <sub>2</sub> DABMe <sub>2</sub>	17	410	**
300	(2-MePh) <sub>2</sub> DABMe <sub>2</sub>	29	320	**

15

\* In the polymer

\*\* Mn characterized by  $^1\text{H}$  NMR.

#### Example 301

20  $\{[(2,6\text{-EtPh})_2\text{DABMe}_2]\text{PdCH}_3(\text{Et}_2\text{O})\}^+\text{SbF}_6^-$  (0.0778g,  
 0.10 mmol) and methyl acrylate (4.78g, 0.056 mol) were  
 dissolved in 40 mL  $\text{CH}_2\text{Cl}_2$  in a Schlenk flask in a  
 drybox. The flask was connected to a Schlenk line and  
 the flask was then briefly evacuated and refilled with  
 25 ethylene from the Schlenk line. This was stirred at RT  
 under 1 atm of ethylene for 72 h. The mixture was  
 filtered through silica gel, solvent was evaporated and  
 then vacuum dried, and 1.92g light of a yellow viscous  
 oil was obtained.  $^1\text{H}$  NMR analysis ( $\text{CDCl}_3$ ): 69 methyls  
 30 per 1000 methylene carbons. Comparison of the integral



of the methyl on the ester groups (2.3 ppm) with the integrals of carbon chain methyls (0.8-1.0 ppm) and methylenes (1.1-1.4 ppm) indicated a comonomer content of 16 mol%. The polymer exhibited a Tg of -68°C by DSC. GPC (THF, polystyrene standard): Mw = 14,300, Mn = 7,430, P/D = 1.93.

#### Example 302

$\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdCH}_2\text{CH}_2\text{CH}_2\text{C(O)OCH}_3\}^+\text{SbF}_6^-$  (0.254g, 0.30 mmol) and  $\text{CH}_2=\text{CHCO}_2\text{CH}_2(\text{CF}_2)_6\text{CF}_3$  (90.2g, 0.20 mol) were dissolved in 150 mL  $\text{CH}_2\text{Cl}_2$  in a flask in the drybox. The flask was connected to a Schlenk line and the flask was then briefly evacuated and refilled with ethylene from the Schlenk line. This was stirred at RT under 1 atm of ethylene for 24 h. The solution was decanted to 1200 mL methanol, resulted formation of oil at the bottom of the flask. The upper layer was decanted, oil dissolved in 150 mL  $\text{CH}_2\text{Cl}_2$ , followed by addition of 1200 mL of methanol. The upper layer was decanted, oil dissolved in 600 mL hexane and filtered through Celite®. Solvent was evaporated, and then vacuum dried, yielding 54.7g of a viscous oil.  $^1\text{H}$  NMR analysis ( $\text{CDCl}_3$ ): 99 methyls per 1000 methylene carbons. Comparison of the integral of the  $\text{CH}_2\text{CF}_2$ - (4.56 ppm) with the integrals of methyls (0.8-1.0 ppm) and methylenes (1.1-1.4 ppm) indicated a comonomer content of 5.5 mol%. The polymer exhibited a Tg of -49°C by DSC. Mw = 131,000, Mn = 81,800.

#### Example 303

$\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdCH}_2\text{CH}_2\text{CH}_2\text{C(O)OCH}_3\}^+\text{SbF}_6^-$  (0.169g, 0.20 mmol) and  $\beta$ -hydroxyethyl acrylate (6.67g, 0.057 mol) were dissolved in 40 mL  $\text{CH}_2\text{Cl}_2$  in a flask in the drybox. The flask was connected to a Schlenk line and the flask was then briefly evacuated and refilled with ethylene from the Schlenk line. This was stirred at RT under 1 atm of ethylene for 45 h. Solvent was evaporated. The residue was dissolved in 100 mL hexane, followed by addition of 400 mL methanol. Upon standing overnight, a second upper layer formed and was

decanted. The oil was dissolved in 60 mL THF, followed by addition of 300 mL water. The upper layer was decanted. The residue was dissolved in 100 mL 1:1  $\text{CH}_2\text{Cl}_2$ /hexane. This was filtered through Celite®. The solvent was evaporated, vacuum dried and 6.13g of a light yellow oil was obtained.  $^1\text{H}$  NMR analysis ( $\text{CD}_2\text{Cl}_2$ ): 142 methyls per 1000 methylene carbons. Comparison of the integral of the  $\text{CH}_2\text{CO}_2$ - (2.30 ppm) with the integrals of methyls (0.8-1.0 ppm) and methylenes (1.1-1.4 ppm) indicated a comonomer content of 2.6 mol%.  $\text{Mw} = 53,100$ ,  $\text{Mn} = 37,900$ ,  $\text{P/D} = 1.40$ .

#### Example 304

$\{[(2,6\text{-i-PrPh})_2\text{DABME}_2]\text{PdCH}_2\text{CH}_2\text{CH}_2\text{C(O)OCH}_3\}^+\text{SbF}_6^-$  (0.169g, 0.20 mmol) and hydroxypropyl acrylate (7.52g, 0.058 mol) were dissolved in 40 mL  $\text{CH}_2\text{Cl}_2$  in a flask in the drybox. The flask was connected to a Schlenk line and the flask was then briefly evacuated and refilled with ethylene from the Schlenk line. This was stirred at RT under 1 atm of ethylene for 72 h. Solvent was evaporated. Eighty mL methanol was added to dissolve the residue, followed by 250 mL water. The upper layer was decanted. The reverse precipitation was repeated one more time. The oil was isolated, vacuum dried, and 1.1g of a light yellow oil was obtained.  $^1\text{H}$  NMR analysis ( $\text{CD}_2\text{Cl}_2$ ): 94 methyls per 1000 methylene carbons. Comparison of the integral of the  $\text{CH}_2\text{CO}_2$ - (2.30 ppm) with the integrals of methyls (0.8-1.0 ppm) and methylenes (1.1-1.4 ppm) indicated a comonomer content of 6.5 mol%.  $\text{Mw} = 39,200$ ,  $\text{Mn} = 28,400$ ,  $\text{P/D} = 1.38$ .

#### Example 305

The complex  $[(2,4,6\text{-MePh})_2\text{DABAN}]\text{NiBr}_2$  was weighed into a glass vial in the dry box (0.0141 g, 0.025 mmol). Cyclopentene was added (3.41 g, 2,000 equivalents/Ni). A solution of MMAO (Akzo Nobel MMAO-3A, modified methylaluminoxane, 25% isobutyl groups in place of methyl groups) was added while stirring (0.75 ml, 1.7 M Al in heptane, 50 equivalents/Ni). Following

addition of the MMAO, the solution was homogeneous. After stirring for several hours, solid polymer started to precipitate. After stirring for 46 hours, the solution was filtered and the solids were washed several times on the filter with pentane. The polymer was dried in vacuo for 12 hours at room temperature to yield 0.66 g polymer (388 turnovers/Ni). The polymer was pressed at 292°C to give a transparent, light gray, tough film. DSC (25 to 300°C, 15°C/min, second heat): T<sub>g</sub> = 104°C, T<sub>m</sub> (onset) = 210°C, T<sub>m</sub> (end) = 285°C, Heat of fusion = 14 J/g. X-ray powder diffraction shows peaks at d-spacings 5.12, 4.60, 4.20, 3.67, and 2.22. <sup>1</sup>H NMR (500 MHz, 155°C, d<sub>4</sub>-o-dichlorobenzene, referenced to downfield peak of solvent = 7.280 ppm): 0.923 (bs, 1.0 H, -CHCH<sub>2</sub>CH-); 1.332 (bs, 2.0 H, -CHCH<sub>2</sub>CH<sub>2</sub>CH-); 1.759 (bs, 4.0 H, -CHCH<sub>2</sub>CH<sub>2</sub>CH- and -CHCH<sub>2</sub>CH<sub>2</sub>CH-); 1.947 (bs, 1.0 H, -CHCH<sub>2</sub>CH-). The assignments are based upon relative integrals and <sup>1</sup>H - <sup>13</sup>C correlations determined by 2D NMR. This spectrum is consistent with an addition polymer with cis-1,3 enchainment of the cyclopentene.

#### Example 306

Cyclopentene was polymerized by [(2,4,6-MePh)<sub>2</sub>DABMe<sub>2</sub>]PdMeCl and MMAO according to Example 305 to give 0.37 g polymer (217 turnovers/Pd). The polymer was pressed at 250°C to give a transparent, light brown, tough film. DSC (25 to 300°C, 15°C/min, second heat): T<sub>g</sub> = 84°C, T<sub>m</sub>(onset) = 175°C, T<sub>m</sub> (end) = 255°C, Heat of fusion = 14 J/g. <sup>1</sup>H NMR (400 MHz, 120°C, d<sub>4</sub>-o-dichlorobenzene, referenced to downfield peak of solvent = 7.280 ppm): 0.90 (bs, 1 H, -CHCH<sub>2</sub>CH-); 1.32 (bs, 2 H, -CHCH<sub>2</sub>CH<sub>2</sub>CH-); 1.72, 1.76 (bs, bs 4 H, -CHCH<sub>2</sub>CH<sub>2</sub>CH- and -CHCH<sub>2</sub>CH<sub>2</sub>CH-); 1.94 (bs, 1 H, -CHCH<sub>2</sub>CH-). The assignments are based upon relative integrals and <sup>1</sup>H - <sup>13</sup>C correlations determined by 2D NMR. This spectrum is consistent with an addition polymer with cis-1,3 enchainment of the cyclopentene.

#### Example 307

Cyclopentene was polymerized by [(2,6-  
FtPh)<sub>2</sub>DABMe<sub>2</sub>]PdMeCl and MMAO according to Example 305  
to give 0.39 g polymer (229 turnovers/Pd). The polymer  
was pressed at 250°C to give a transparent, light  
5 brown, tough film. DSC (25 to 300°C, 15°C/min, second  
heat): T<sub>g</sub> = 88°C, T<sub>m</sub>(onset) = 175°C, T<sub>m</sub> (end) = 255°C,  
Heat of fusion = 16 J/g. <sup>1</sup>H NMR (300 MHz, 120°C, d<sub>4</sub>-o-  
dichlorobenzene) is very similar to the spectrum of  
Example 306.

10

Example 308

Cyclopentene was polymerized by [(2,4,6-  
MePh)<sub>2</sub>DABMe<sub>2</sub>]NiBr<sub>2</sub> and MMAO according to Example 305 to  
give 0.36 g polymer (211 turnovers/Ni). The polymer  
was pressed at 250°C to give a transparent, colorless,  
15 tough film. DSC (25 to 300°C, 15°C/min, second heat):  
T<sub>g</sub> = 98°C, T<sub>m</sub>(onset) = 160°C, T<sub>m</sub> (end) = 260°C, Heat of  
fusion = 22 J/g. <sup>1</sup>H NMR (500 MHz, 120 °C, d<sub>4</sub>-o-  
dichlorobenzene) is very similar to the spectrum of  
Example 306. X-ray powder diffraction shows the same  
20 crystalline phase as observed in Example 305.

Example 309

Cyclopentene was polymerized by [(2,6-i-  
PrPh)<sub>2</sub>DABMe<sub>2</sub>]PdMeCl and MMAO according to Example 305  
to give 0.73 g of fine powder (429 turnovers/Pd). The  
25 polymer was pressed at 250°C to give a transparent,  
light brown tough film. DSC (25 to 300°C, 15°C/min,  
second heat): T<sub>g</sub> = 96°C, T<sub>m</sub>(onset) = 175°C, T<sub>m</sub> (end) =  
250°C, Heat of fusion = 14 J/g. <sup>1</sup>H NMR (400 MHz, 120°C,  
d<sub>4</sub>-o-dichlorobenzene) is very similar to the spectrum  
30 of Example 306. X-ray powder diffraction shows the  
same crystalline phase as observed in Example 305.

Example 310

Cyclopentene was polymerized by [(2,6-i-  
PrPh)<sub>2</sub>DABMe<sub>2</sub>]PdCl<sub>2</sub> and MMAO according to Example 305 to  
35 give 0.856 g polymer (503 turnovers/Pd). The polymer  
was pressed at 250°C to give a transparent, light  
brown, tough film. DSC (25 to 300°C, 15°C/min, second  
heat): T<sub>g</sub> = 104°C, T<sub>m</sub>(onset) = 140°C, T<sub>m</sub> (end) = 245°C,

Heat of fusion = 19 J/g.  $^1\text{H}$  NMR (400 MHz, 120°C,  $\text{d}_4$ -o-dichlorobenzene) is very similar to the spectrum of Example 306.

Example 311

5       Cyclopentene was polymerized by [(2,6-EtPh) $_2$ DABMe $_2$ ]NiBr $_2$  and MMAO according to Example 305 to give 0.076 g polymer (45 turnovers/Ni).  $^1\text{H}$  NMR (400 MHz, 120°C,  $\text{d}_4$ -o-dichlorobenzene) is very similar to the spectrum of Example 306.

10       Example 312

Cyclopentene was polymerized by [(2,4,6-MePh) $_2$ DABH $_2$ ]NiBr $_2$  and MMAO according to Example 305 to give 0.66 g polymer (388 turnovers/Ni). The polymer was pressed at 292°C to give a tough film.  $^1\text{H}$  NMR (400  
15 MHz, 120°C,  $\text{d}_4$ -o-dichlorobenzene) is very similar to the spectrum of Example 306. A DSC thermal fractionation experiment was done in which a sample was heated to 330°C at 20°C/minute followed by stepwise isothermal equilibration at the followed temperatures  
20 (times): 280°C (6 hours), 270°C (6 hours), 260°C (6 hours), 250°C (6 hours), 240°C (4 hours), 230°C (4 hours), 220°C (4 hours), 210°C (4 hours), 200°C (3 hours), 190°C (3 hours), 180°C (3 hours), 170°C (3 hours), 160°C (3 hours), 150°C (3 hours). The DSC of  
25 this sample was then recorded from 0°C - 330°C at 10°C/min. T $_g$  = 98°C, T $_m$  (onset) = 185°C, T $_m$  (end) = 310°C, Heat of fusion = 35 J/g.

Example 313

Cyclopentene was polymerized by [(2-PhPh) $_2$ DABMe $_2$ ]NiBr $_2$  and MMAO according to Example 305 to  
30 give 1.24 g polymer (728 turnovers/Ni). The polymer was pressed at 292°C to give a transparent, light gray, brittle film. DSC (25 to 320°C, 10°C/min, second heat): T $_m$ (onset) = 160°C, T $_m$  (end) = 285°C, Heat of  
35 fusion = 33 J/g.  $^1\text{H}$  NMR (400 MHz, 120°C,  $\text{d}_4$ -o-dichlorobenzene) is very similar to the spectrum of Example 306. Several peaks attributed to cyclopentenyl end groups were observed in the range 5.2-5.7 ppm.

Integration of these peaks was used to calculate  $M_n = 13,900$ . IR (pressed film,  $\text{cm}^{-1}$ ): 3050 (vw, olefinic end group, CH stretch), 1615 (vw, olefinic end group, cis-CH=CH- double bond stretch), 1463 (vs), 1445 (vs), 1362 (s), 1332 (s), 1306 (s), 1253 (m), 1128 (w), 1041 (w), 935 (m), 895 (w), 882 (w), 792 (w), 721 (w, olefinic end group, cis-CH=CH-, CH bend). GPC (Dissolved in 1,2,4-trichlorobenzene at  $150^\circ\text{C}$ , run at  $100^\circ\text{C}$  in tetrachloroethylene, polystyrene calibration): Peak MW = 13,900;  $M_n = 10,300$ ;  $M_w = 17,600$ ;  $M_w/M_n = 1.70$ .

#### Example 314

The complex  $[(2,4,6\text{-MePh})_2\text{DABAn}]\text{NiBr}_2$  was weighed into a glass vial in the dry box (0.032 g, 0.050 mmol). Toluene (2.35 ml) and cyclopentene (6.81 g, 2,000 equivalents/Ni) were added, followed by  $\text{C}_6\text{H}_5\text{NHMe}_2^+ \text{B}(\text{C}_6\text{F}_5)_4^-$  (0.04 g, 50 equivalents/Ni). A solution of  $\text{Et}_3\text{Al}$  was added while stirring (2.5 ml, 1 M in heptane, 50 equivalents/Ni). After stirring for 46 hours, the solution was filtered and the solids were washed several times on the filter with pentane. The polymer was dried in vacuo for 12 hours at room temperature to yield 0.16 g of fine powder (47 turnovers/Ni). A control experiment with no  $\text{C}_6\text{H}_5\text{NHMe}_2^+ \text{B}(\text{C}_6\text{F}_5)_4^-$  gave no polymer.

#### Example 315

The complex  $[(2,4,6\text{-MePh})_2\text{DABAn}]\text{NiBr}_2$  was weighed into a glass vial in the dry box (0.032 g, 0.050 mmol). Toluene (3.46 ml) and cyclopentene (6.81 g, 2,000 equivalents/Ni) were added. A solution of  $\text{Et}_2\text{AlCl}$  was added while stirring (1.39 ml, 1.8 M in toluene, 50 equivalents/Ni). After stirring for 46 hours, the solution was filtered and the solids were washed several times on the filter with pentane. The polymer was dried in vacuo for 12 hours at room temperature to yield 0.53 g of fine powder (156 turnovers/Ni).

#### Example 316

The complex  $[(2,4,6\text{-MePh})_2\text{DABMe}_2]\text{NiBr}_2$  was weighed into a glass vial in the dry box (0.0070 g, 0.0130

mmol). Pentane (2.2 ml) and cyclopentene (10.0 g, 11,300 equivalents/Ni) were added. A solution of EtAlCl<sub>2</sub> was added while stirring (0.73 ml, 1.0 M in hexanes, 56 equivalents/Ni). After stirring for 192 hours, the solution was filtered and the solids were washed several times on the filter with pentane. The polymer was dried in vacuo for 12 hours at room temperature to yield 2.66 g of fine powder (3010 turnovers/Ni). The polymer was mixed with 200 ml of MeOH in a blender at high speed to produce a fine powder. The solid was collected by filtration and then mixed for 1 hour with 39 ml of a 1:1 mixture of MeOH/concentrated aqueous HCl. The solid was collected by filtration, washed with distilled water, and then washed on the filter 3X with 20 ml of a 2 wt. % solution of Irganox® 1010 in acetone. The polymer was dried in vacuo for 12 hours at room temperature. DSC (25 to 300°C, 10°C/min, controlled cool at 10°C/min, second heat): T<sub>g</sub> = 98°C, T<sub>m</sub>(onset) = 160°C, T<sub>m</sub>(end) = 240°C, Heat of fusion = 17 J/g. TGA(air, 10°C/min): T(onset of loss) = 330°C. T(10% loss) = 450°C. <sup>13</sup>C NMR (500 MHz <sup>1</sup>H frequency, 3.1 ml of 1,2,4-trichlorobenzene, 0.060g Cr(acac)<sub>3</sub>, 120°C): 30.640 (s, 2C), 38.364 (s, 1C), 46.528 (s, 2C). This spectrum is consistent with an addition polymer of cyclopentene with cis-1,3-enchainment. A sample of the polymer was melted in a Schlenk tube under a nitrogen atmosphere. Fibers were drawn from the molten polymer using a stainless steel cannula with a bent tip. A nitrogen purge was maintained during the fiber drawing. The fibers were tough and could be drawn about 2X by pulling against a metal surface heated to 125°C.

#### Example 317

The complex [(2,4,6-MePh)<sub>2</sub>DABAN]NiBr<sub>2</sub> was weighed into a glass vial in the dry box (0.0093 g, 0.0146 mmol). Cyclopentene (10.0 g, 10,000 equivalents/Ni) was added. A solution of EtAlCl<sub>2</sub> was added while stirring (0.73 ml, 1.0 M in hexanes, 50

equivalents/Ni). After stirring for 168 hours, the solution was filtered and the solids were washed several times on the filter with pentane. The polymer was dried in vacuo for 12 hours at room temperature to yield 4.66 g of fine powder (4660 turnovers/Ni). The polymer was mixed with 200 ml of MeOH in a blender at high speed to produce a fine powder. The solid was collected by filtration and then mixed for 1 hour with 39 ml of a 1:1 mixture of MeOH/concentrated aqueous HCl. The solid was collected by filtration, washed with distilled water, and then washed on the filter 3X with 20 ml of a 2 wt. % solution of Irganox 1010 in acetone. The polymer was dried in vacuo for 12 hours at room temperature. DSC (25 to 350°C, 15°C/min, second heat):  $T_g = 97^\circ\text{C}$ ,  $T_m(\text{onset}) = 160^\circ\text{C}$ ,  $T_m(\text{end}) = 285^\circ\text{C}$ , Heat of fusion = 25 J/g.  $^{13}\text{C}$  NMR (500 MHz  $^{13}\text{H}$  frequency, 3.1 ml of 1,2,4-trichlorobenzene, 0.060g  $\text{Cr}(\text{acac})_3$ , 120°C): 30.604 (s, 2C), 38.333 (s, 1C), 46.492 (s, 2C). This spectrum is consistent with an addition polymer of cyclopentene with cis-1,3-enchainment. A sample of the polymer was melted in a Schlenk tube under a nitrogen atmosphere. Fibers were drawn from the molten polymer using a stainless steel cannula with a bent tip. A nitrogen purge was maintained during the fiber drawing. The fibers were tough and could be drawn about 2X by pulling against a metal surface heated to 125 °C. GPC (Dissolved in 1,2,4-trichlorobenzene at 150°C, run at 100°C in tetrachloroethylene, polystyrene calibration): Peak MW = 137,000;  $M_n = 73,000$ ;  $M_w = 298,000$ ;  $M_w/M_n = 4.08$ .

#### Example 318

The complex  $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdMe}(\text{Et}_2\text{O})\}^+\text{SbF}_6^-$  (0.05 g, 0.060 mmol) was added to 10.0 g of stirring cyclopentene. Solid polymer formed rapidly and precipitated. The polymer was isolated by filtration, washed on the filter 3X with pentane, and dried in vacuo at room temperature to give 1.148 g finely divided powder (282 turnovers/Pd). DSC (25 to 350°C,



15°C/min, first heat):  $T_m(\text{onset}) = 175^\circ\text{C}$ ,  $T_m(\text{end}) = 215^\circ\text{C}$ , Heat of fusion = 16 J/g.

Example 319

The complex  $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdCH}_2\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OCH}_3\}^+\text{SbF}_6^-$  (0.05 g, 0.059 mmol) was added to 10.0 g of stirring cyclopentene. The complex is not very soluble in cyclopentene. The amount of solids increased slowly. After 27 days, the solid polymer was isolated by filtration, washed on the filter 3X with pentane, and dried in vacuo at room temperature to give 1.171 g finely divided powder (292 turnovers/Pd). DSC (25 to 350°C, 15°C/min, first heat):  $T_m(\text{onset}) = 170^\circ\text{C}$ ,  $T_m(\text{end}) = 255^\circ\text{C}$ , Heat of fusion = 24 J/g.

Example 320

The complex  $[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{NiBr}_2$  was weighed into a glass vial in the dry box (0.025 g, 0.040 mmol). Cyclopentene (10.0 g, 1,000 equivalents/Ni) was added. A solution of MMAO was added while stirring (0.802 ml, 2.5 M in heptane, 50 equivalents/Ni). After stirring for 5 minutes, the mixture was rusty brown and still contained some solids. An additional 50 equivalents of MMAO were added and the solution became homogeneous. After 12 hours, the mixture was filtered and the solids were washed several times on the filter with pentane. The polymer was dried in vacuo for 12 hours at room temperature to yield 0.238 g of fine powder (87 turnovers/Ni). DSC (25 to 350°C, 15°C/min, second heat):  $T_m(\text{onset}) = 170^\circ\text{C}$ ,  $T_m(\text{end}) = 265^\circ\text{C}$ , Heat of fusion = 18 J/g.

Example 321

The complex  $[(2,4,6\text{-MePh})_2\text{DABAn}]\text{NiBr}_2$  was weighed into a glass vial in the dry box (0.0093 g, 0.0146 mmol). Cyclopentene (10.0 g, 10,000 equivalents/Ni) and anhydrous methylene chloride (48.5 ml) were added. A solution of  $\text{EtAlCl}_2$  was added while stirring (2.92 ml, 1.0 M in toluene, 200 equivalents/Ni). After stirring for 163 hours, the solution was filtered and

the solids were washed several times on the filter with pentane. The polymer was dried in vacuo for 12 hours at room temperature to yield 1.64 g of fine powder (1640 turnovers/Ni). A DSC thermal fractionation experiment was done according to the procedure of Example 312. A DSC was then recorded from 0°C to 330°C at 10°C/min.  $T_g = 92^\circ\text{C}$ ,  $T_m$  (onset) =  $150^\circ\text{C}$ ,  $T_m$  (end) =  $250^\circ\text{C}$ , Heat of fusion = 11.4 J/g.

#### Example 322

The complex  $[(2,4,6\text{-MePh})_2\text{DABAN}]\text{NiBr}_2$  was weighed into a glass vial in the dry box (0.0093 g, 0.0146 mmol). Cyclopentene (10.0 g, 10,000 equivalents/Ni) was added. A solution of  $i\text{-BuAlCl}_2$  was added while stirring (2.92 ml, 1.0 M in toluene, 200 equivalents/Ni). After stirring for 163 hours, the solution was filtered and the solids were washed several times on the filter with pentane. The polymer was dried in vacuo for 12 hours at room temperature to yield 1.99 g of fine powder (1990 turnovers/Ni). The polymer was pressed at  $292^\circ\text{C}$  to give a transparent, light gray, tough film. A DSC thermal fractionation experiment was done according to the procedure of Example 312. A DSC was then recorded from 0°C to  $330^\circ\text{C}$  at 10 °C/min.  $T_g = 103^\circ\text{C}$ ,  $T_m$  (onset) =  $150^\circ\text{C}$ ,  $T_m$  (end) =  $290^\circ\text{C}$ , Heat of fusion = 27 J/g.

#### Example 323

The complex  $[(2,4,6\text{-MePh})_2\text{DABAN}]\text{NiBr}_2$  was weighed into a glass vial in the dry box (0.0932 g, 0.146 mmol). Cyclopentene (5.0 g, 500 equivalents/Ni) and toluene (6.54 ml) were added. A solution of PMAO (Akzo Nobel Polymethylaluminoxane) was added while stirring (3.16 ml, 2.32 M Al in toluene, 50 equivalents/Ni). After stirring for 163 hours, the solution was filtered and the solids were washed several times on the filter with pentane. The polymer was dried in vacuo for 12 hours at room temperature to yield 3.64 g of fine powder (364 turnovers/Ni). The polymer was pressed at  $292^\circ\text{C}$  to give a brown film that seemed tough, but

failed along a straight line when it broke. A DSC thermal fractionation experiment was done according to the procedure of Example 312 was then recorded from 0°C to 330°C at 10°C/min.  $T_g = 100^\circ\text{C}$ ,  $T_m$  (onset) =  $150^\circ\text{C}$ ,  
5  $T_m$  (end) =  $270^\circ\text{C}$ , Heat of fusion = 21 J/g.

#### Example 324

A mixture of 20mg (0.032mmol) of  $\text{NiBr}_2[(2,6\text{-i-PrPh})_2\text{DABMe}_2]$  was magnetically-stirred under nitrogen in a 50-mL Schlenk flask with 15mL of dry, deaerated  
10 toluene as 0.6mL of 3M poly(methylalumoxane) was injected via syringe. The mixture became deep blue-black. Then 2.5mL (14mmol) of beta-citronellene,  $(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}=\text{CH}_2$ , was injected and the mixture was immediately pressurized with ethylene at  
15 190 kPa (absolute) and was stirred at  $23^\circ\text{C}$  for 17h; by the end of 17h, the solution was too thick to stir. The ethylene was vented and the toluene solution was stirred with 6N HCl and methanol and was decanted. The polymer was stirred with refluxing methanol for an hour  
20 to extract solvent; oven-drying yielded 0.90g of rubbery polyethylene.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) showed a  $\text{CH}_2:\text{CH}_3$  ratio of 83:12, which is 101  $\text{CH}_3$ 's per 1000  $\text{CH}_2$ 's; there were small peaks for the beta-citronellene isopropylidene dimethyls (1.60 and 1.68ppm), as well as  
25 a tiny peak for vinyl H (5.0ppm); diene incorporation was estimated at 0.7mol%. Differential scanning calorimetry:  $-51^\circ\text{C}$  ( $T_g$ ). GPC data (trichlorobenzene,  $135^\circ\text{C}$ ; PE standard):  $M_n=23,200$ ;  $M_w=79,200$ ;  $M_z=154,000$ ;  $M_w/M_n=3.42$ .

#### 30 Example 325

A 15-mg (0.024-mmol) sample of  $\text{NiBr}_2[(2,6\text{-i-PrPh})_2\text{DABMe}_2]$  was magnetically stirred under nitrogen in a 50-mL Schlenk flask with 25mL of dry, deaerated toluene and 5mL (27mmol) of dry, deaerated 1,9-  
35 decadiene. Then 0.6mL of polymethylalumoxane (1.7M MAO in heptane; contains about 30% isobutyl groups) was injected; the tan suspension did not change color. The mixture was pressurized with ethylene to 190 kPa

(absolute) and was stirred for 1hr; it began to grow green-gray and darker in color, so 0.6mL more MAO was added, after which the mixture soon turned deep green-black. The reaction was stirred for 16hr and the ethylene was then vented; by this time the solution had become thick and unstirrable. The mixture was stirred with refluxing 6N HCl and methanol, and the polymer was washed with methanol, pressed free of solvent, and dried under high vacuum to yield 1.0g of rubbery polyethylene. The polymer was insoluble in hot dichlorobenzene, demonstrating incorporation of the diene.

#### Example 326

A 21-mg (0.034-mmol) sample of  $\text{NiBr}_2[(2,6\text{-i-PrPh})_2\text{DABMe}_2]$  was magnetically stirred under nitrogen in a 50-mL Schlenk flask with 25mL of dry, deaerated toluene. Then 0.6mL of 2.9M polymethylalumoxane was injected; the red-brown suspension became deep green. The mixture was purged with ethylene and then 2.0mL (1.4g; 15mmol) of 2-methyl-1,5-hexadiene was added; the mixture was pressurized with ethylene to 190 kPa and was stirred for 18h; the solution became brown. The ethylene was vented and the toluene solution was stirred with 6N HCl and methanol and was separated; rotary evaporation of the toluene layer yielded, after acetone washing to remove catalyst, 47mg of viscous liquid polymer.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) showed a  $\text{CH}_2:\text{CH}_3$  ratio of 82:15, which is 130  $\text{CH}_3$ 's per 1000  $\text{CH}_2$ 's. There were also peaks for the incorporated diene at 1.72ppm (0.5H;  $\text{CH}_3\text{-C=CH}_2$ ) and 4.68ppm (0.3H;  $\text{CH}_3\text{-C=CH}_2$ ) and no evidence of terminal vinyl ( $\text{-CH=CH}_2$ ; 4.95 and 5.80ppm) from unincorporated diene. The level of diene incorporation was about 0.7mol%.

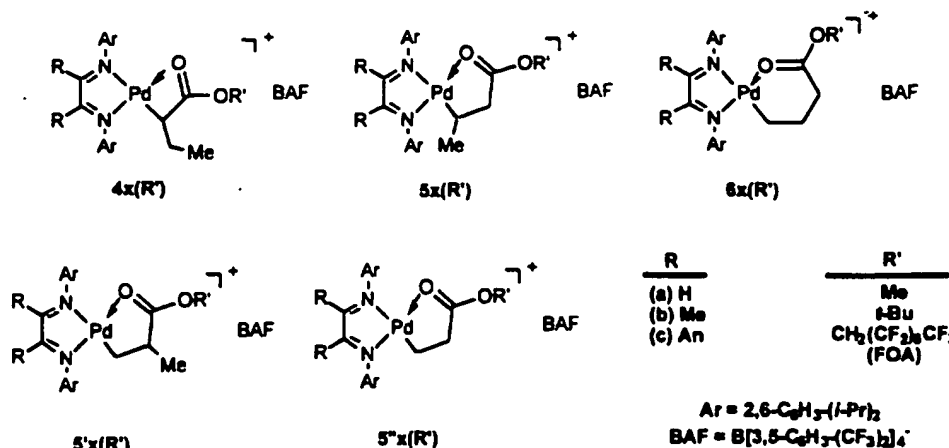
#### Example 327

A 30-mg (0.049-mmol) sample of  $\text{NiBr}_2[(2,6\text{-i-PrPh})_2\text{DABMe}_2]$  was magnetically stirred under nitrogen in a 50-mL Schlenk flask with 25mL of dry, deaerated toluene. Then 1.0mL of methylalumoxane (1.7M in

heptane; contains about 30% isobutyl groups) was injected; the red-brown suspension became deep green. The mixture was saturated with ethylene and then 0.5mL (0.38g; 3.0mmol) of 2-methyl-2,7-octadiene was added; 5 the mixture was pressurized with ethylene to 190 kPa (absolute) and was stirred for 18h; the solution became brown. The ethylene was vented and the toluene solution was stirred with 6N HCl and methanol and was separated; rotary evaporation of the toluene yielded, 10 after acetone washing to remove catalyst, 0.15g of viscous liquid polymer.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) showed a  $\text{CH}_2:\text{CH}_3$  ratio of 81.5:13.5, which is 117  $\text{CH}_3$ 's per 1000  $\text{CH}_2$ 's. The level of diene incorporation was about 0.5-1.0mol%, judging from the diene isopropylidene methyls 15 at 1.60 and 1.69ppm.

Examples 328-335

Acrylate Chelate Complexes. The chelate complexes for these examples were generated in situ for NMR studies by the reaction of  $[(\text{ArN}=\text{C}(\text{R})-\text{C}(\text{R})=\text{NAr})\text{PdMe}(\text{OEt}_2)]\text{BAF}$  with  $\text{H}_2\text{C}=\text{CHC}(\text{O})\text{OR}'$  and on a 20 preparative scale by the reaction of NaBAF with  $(\text{ArN}=\text{C}(\text{R})-\text{C}(\text{R})=\text{NAr})\text{PdMeCl}$  and  $\text{H}_2\text{C}=\text{CHC}(\text{O})\text{OR}'$  (*vide infra*). In these examples, the following labeling scheme is used to identify the different chelate 25 complexes that were observed and/or isolated. Assignments of all  $^1\text{H}$  NMR chelate resonances were confirmed by homonuclear decoupling experiments.



### General Procedure for the Synthesis of Chelate Complexes

- A gastight microliter syringe was used to add 1.1 equiv of  $H_2C=CHC(O)OR'$  to a mixture of 1 equiv of NaBAF and 1 equiv of  $[(2,6-i-PrPh)_2DABR_2]PdMeCl$  suspended in 25 mL of  $Et_2O$ . The sides of the Schlenk flask were rinsed with an additional 25 mL of  $Et_2O$  and the reaction mixture was stirred for 1-2 days at RT.
- Sodium chloride was removed from the reaction mixture via filtration, yielding a clear orange solution. The  $Et_2O$  was removed in vacuo and the product was washed with hexane and dried in vacuo. For  $R' = Me$  or  $t-Bu$ , no further purification was necessary (yields > 87%).
- Recrystallization lowered the yield of product and did not result in separation of the isomeric mixtures.

- For  $R' = -CH_2(CF_2)_6CF_3$ , contamination of the product with unreacted NaBAF was sometimes observed. Filtration of a  $CH_2Cl_2$  solution of the product removed the NaBAF. The  $CH_2Cl_2$  was then removed in vacuo to yield a partially oily product. A brittle foam was obtained by dissolving the product in  $Et_2O$  and removing the  $Et_2O$  in vacuo (yields > 59%). Although isolable, chelate complexes derived from FOA tended to be less stable than those derived from MA or  $t-BuA$  and decomposed with time or additional handling.

Spectral Data for the BAF Counterion The following  $^1H$  and  $^{13}C$  spectroscopic assignments of the BAF counterion in  $CD_2Cl_2$  were invariant for different

complexes and temperatures and are not repeated in the spectroscopic data for each of the cationic complexes: (BAF).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  7.74 (s, 8,  $\text{H}_\text{O}$ ), 7.57 (s, 4,  $\text{H}_\text{P}$ );  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  162.2 (q,  $\text{JCB} = 37.4$ ,  $\text{Cipso}$ ), 135.2 ( $\text{C}_\text{O}$ ), 129.3 (q,  $\text{JCF} = 31.3$ ,  $\text{C}_\text{m}$ ), 125.0 (q,  $\text{JCF} = 272.5$ ,  $\text{CF}_3$ ), 117.9 ( $\text{C}_\text{p}$ ).

#### Example 328

The above synthesis using [(2,6-i-PrPh) $_2$ DABH $_2$ ]PdMeCl (937 mg, 1.76 mmol), NaBAF (1.56 g, 1.75 mmol), and MA (175  $\mu\text{L}$ , 1.1 equiv) was followed and the reaction mixture was stirred for 12 h. The resulting orange powder (2.44 g, 96.0%) consisted of a mixture of 6a(Me) (91%), 5'a(Me) (5%), and 5a(Me) (4%), according to  $^1\text{H}$  NMR spectroscopy. 6a(Me):  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 400 MHz, rt)  $\delta$  8.31 and 8.26 (s, 1 each,  $\text{N}=\text{C}(\text{H})-\text{C}'(\text{H})=\text{N}$ ), 7.5 - 7.2 (m, 6,  $\text{H}_\text{aryl}$ ), 3.17 (s, 3, OMe), 3.14 and 3.11 (septet, 2 each,  $\text{CHMe}_2$  and  $\text{C}'\text{HMe}_2$ ), 2.48 (t, 2,  $\text{J} = 5.8$ ,  $\text{CH}_2\text{C}(\text{O})$ ), 1.75 (t, 2,  $\text{J} = 5.8$ ,  $\text{PdCH}_2$ ), 1.38, 1.32, 1.25 and 1.22 (d, 6 each,  $\text{J} = 6.8$ ,  $\text{CHMeMe}'$  and  $\text{C}'\text{HMeMe}'$ ), 0.73 (pentet, 2,  $\text{J} = 5.8$ ,  $\text{PdCH}_2\text{CH}_2\text{CH}_2\text{C}(\text{O})$ );  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 100 MHz, rt)  $\delta$  183.9 ( $\text{C}(\text{O})$ ), 167.1 ( $\text{JCH} = 181.4$ ,  $\text{N}=\text{C}(\text{H})$ ), 160.7 ( $\text{JCH} = 181.3$ ,  $\text{N}=\text{C}'(\text{H})$ ), 142.9 and 142.4 ( $\text{Ar}$ ,  $\text{Ar}'$ :  $\text{Cipso}$ ), 139.7 and 138.7 ( $\text{Ar}$ ,  $\text{Ar}'$ :  $\text{Cipso}$ ), 129.8 and 129.0 ( $\text{Ar}$ ,  $\text{Ar}'$ :  $\text{Cp}$ ), 124.6 and 124.1 ( $\text{Ar}$ ,  $\text{Ar}'$ :  $\text{C}_\text{m}$ ), 55.2 (OMe), 35.9 and 32.3 ( $\text{PdCH}_2\text{CH}_2\text{CH}_2\text{C}(\text{O})$ ), 29.3 and 29.1 ( $\text{CHMe}_2$ ,  $\text{C}'\text{HMe}_2$ ), 23.8 ( $\text{PdCH}_2\text{CH}_2\text{CH}_2\text{C}(\text{O})$ ), 24.5, 23.9, 23.2 and 22.5 ( $\text{CHMeMe}'$ ,  $\text{C}'\text{HMeMe}'$ ); IR ( $\text{CH}_2\text{Cl}_2$ )  $1640\text{ cm}^{-1}$  [ $\nu(\text{C}(\text{O}))$ ]. 5'a(Me):  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 100 MHz, rt)  $\delta$  193.2 ( $\text{C}(\text{O})$ ). Anal. Calcd for ( $\text{C}_{63}\text{H}_{57}\text{BF}_{24}\text{N}_2\text{O}_2\text{Pd}$ ): C, 52.28; H, 3.97; N, 1.94. Found: C, 52.08; H, 3.75; N, 1.61.

#### Example 329

The above synthesis using [(2,6-i-PrPh) $_2$ DABMe $_2$ ]PdMeCl (634 mg, 1.13 mmol), NaBAF (1.00 g, 1.13 mmol), and MA (112  $\mu\text{L}$ , 1.1 equiv) was followed. The reaction mixture was stirred for 2 days and the product was recrystallized from  $\text{CH}_2\text{Cl}_2$  at  $-30^\circ\text{C}$  to

give 956 mg of orange crystals (57.3%, 2 crops). The crystals consisted of a mixture of **6b(Me)** (87%), **5'b(Me)** (11.5%), and **5b(Me)** (1.5%), according to  $^1\text{H}$  NMR spectroscopy. **6b(Me)**:  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 400 MHz, rt)  $\delta$  7.43 - 7.26 (m, 6,  $\text{H}_{\text{aryl}}$ ), 3.03 (s, 3, OMe), 2.95 (septet, 2,  $J = 6.79$ ,  $\text{CHMe}_2$ ), 2.93 (septet, 2,  $J = 6.83$ ,  $\text{C}'\text{HMe}_2$ ), 2.39 (t, 2,  $J = 5.86$ ,  $\text{CH}_2\text{C}(\text{O})$ ), 2.22 and 2.20 ( $\text{N}=\text{C}(\text{Me})-\text{C}'(\text{Me})=\text{N}$ ), 1.41 (t, 2,  $J = 5.74$ ,  $\text{PdCH}_2$ ), 1.37, 1.30, 1.25 and 1.21 (s, 6 each,  $J = 6.80$  - 6.94,  $\text{CHMeMe}'$ ,  $\text{C}'\text{HMeMe}'$ ), 0.66 (pentet, 2,  $J = 5.76$ ,  $\text{PdCH}_2\text{CH}_2\text{CH}_2\text{C}(\text{O})$ );  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 100 MHz, rt)  $\delta$  183.4 ( $\text{C}(\text{O})$ ), 178.7 and 171.6 ( $\text{N}=\text{C}-\text{C}'=\text{N}$ ), 140.8 and 140.5 ( $\text{Ar}$ ,  $\text{Ar}'$ : Cipso), 138.6 and 138.0 ( $\text{Ar}$ ,  $\text{Ar}'$ :  $\text{C}_\text{O}$ ), 129.3 and 128.3 ( $\text{Ar}$ ,  $\text{Ar}'$ :  $\text{C}_\text{p}$ ), 124.9 and 124.4 ( $\text{Ar}$ ,  $\text{Ar}'$ :  $\text{C}_\text{m}$ ), 54.9 (OMe), 35.8 and 30.3 ( $\text{PdCH}_2\text{CH}_2\text{CH}_2\text{C}(\text{O})$ ), 29.5 and 29.2 ( $\text{CHMe}_2$ ,  $\text{C}'\text{HMe}_2$ ), 23.7 ( $\text{PdCH}_2\text{CH}_2\text{CH}_2\text{C}(\text{O})$ ), 23.91, 23.86, 23.20 and 23.14 ( $\text{CHMeMe}'$ ,  $\text{C}'\text{HMeMe}'$ ), 21.6 and 19.9 ( $\text{N}=\text{C}(\text{Me})-\text{C}'(\text{Me})=\text{N}$ ); IR ( $\text{CH}_2\text{Cl}_2$ )  $1643\text{ cm}^{-1}$  [ $\nu(\text{C}(\text{O}))$ ]. **5'b(Me)**:  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 400 MHz, rt)  $\delta$  3.47 (s, 3, OMe), 2.54 (m, 1,  $\text{CHMeC}(\text{O})$ ), 2.19 and 2.18 (s, 3 each,  $\text{N}=\text{C}(\text{Me})-\text{C}'(\text{Me})=\text{N}$ ), 1.02 (d, 3,  $J = 7.23$ ,  $\text{CHMeC}(\text{O})$ );  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 100 MHz, rt)  $\delta$  194.5 ( $\text{C}(\text{O})$ ), 179.2 and 172.2 ( $\text{N}=\text{C}-\text{C}'=\text{N}$ ), 55.6 (OMe), 44.3 ( $\text{CHMeC}(\text{O})$ ), 28.4 ( $\text{PdCH}_2$ ), 21.2 and 19.6 ( $\text{N}=\text{C}(\text{Me})-\text{C}'(\text{Me})=\text{N}$ ), 18.1 ( $\text{CHMeC}(\text{O})$ ). **5b(Me)**:  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 400 MHz, rt)  $\delta$  0.26 (d, 3,  $\text{PdCHMe}$ ). Anal. Calcd for ( $\text{C}_{65}\text{H}_{61}\text{BF}_{24}\text{N}_2\text{O}_2\text{Pd}$ ): C, 52.92; H, 4.17; N, 1.90. Found: C, 52.91; H, 4.09; N, 1.68.

#### Example 330

The above synthesis was followed using [(2,6-*i*-PrPh) $_2$ DABAn] $\text{PdMeCl}$  (744 mg, 1.13 mmol), NaBAF (1.00 g, 1.13 mmol), and MA (112  $\mu\text{L}$ , 1.1 equiv). The reaction mixture was stirred for 2 days and the product was recrystallized from  $\text{CH}_2\text{Cl}_2$  at  $-30^\circ\text{C}$  to give 600 mg (33.8%, 2 crops) of a mixture of **6c(Me)** (85%), **5'c(Me)** (8%), **5''c(Me)** (6%), and **5c(Me)** (1%), according to  $^1\text{H}$  NMR spectroscopy. **6c(Me)**:  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ) 400 MHz, rt)  $\delta$  8.17 (d, 1,  $J = 8.37$ , An:  $\text{H}_\text{p}$ ), 8.15 (d, 1,  $J =$



- 3.49, An': H'p), 7.62 - 7.40 (m, 8, An, An': Hm, H'm; Ar: Hm, Hp; Ar': H'm, H'p), 7.08 (d, 1, J = 7.19, An: HO), 6.60 (d, 1, J = 7.44, An': H'O), 3.37 (septet, 2, J = 6.79, CHMe<sub>2</sub>), 3.33 (septet, 2, J = 6.86, C'HMe<sub>2</sub>), 2.55 (t, 2, J = 5.93, CH<sub>2</sub>C(O)), 1.79 (t, 2, J = 5.66, PdCH<sub>2</sub>), 1.45, 1.42, 1.13 and 1.02 (d, 6 each, J = 6.79 - 6.90, CHMeMe', C'HMeMe'), 0.80 (pentet, 2, J = 5.82, PdCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C(O)); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100 MHz, rt) δ 183.5 (C(O)), 175.3 and 168.7 (N=C-C'=N), 145.9 (An: quaternary C), 141.3 and 140.5 (Ar, Ar': Cipso), 139.7 and 138.4 (Ar, Ar': CO), 133.3 and 132.6 (An: CH), 131.9 (An: quaternary C), 129.8, 129.7, 129.6 and 128.5 (Ar, Ar': Cp; An: CH), 126.44 and 125.8 (An: quaternary C), 126.4 and 125.6 (An: CH), 125.5 and 124.6 (Ar, Ar': Cm), 55.0 (OMe), 35.9 and 31.3 (PdCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C(O)), 29.7 and 29.4 (CHMe<sub>2</sub>, C'HMe<sub>2</sub>), 24.1 (PdCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C(O)), 24.1, 23.8, 23.32 and 23.27 (CHMeMe', C'HMeMe'); IR (CH<sub>2</sub>Cl<sub>2</sub>) 1644 cm<sup>-1</sup> [ν(C(O))]. 5'c(Me): <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz, rt) δ 3.64 (s, 3, OMe), 2.70 (m, 1, CHMeC(O)); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100 MHz, rt) δ 192.8 (C(O)). 5''c(Me): <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz, rt) δ 3.67 (s, 3, OMe), 2.46 (t, 2, J = 6.99, CH<sub>2</sub>C(O)), 1.72 (t, 2, J = 7.04, PdCH<sub>2</sub>). 5c(Me): <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz, rt) δ 0.44 (d, 3, PdCHMe).
- 25 Anal. Calcd for (C<sub>73</sub>H<sub>61</sub>BF<sub>24</sub>N<sub>2</sub>O<sub>2</sub>Pd): C, 55.80; H, 3.91; N, 1.78. Found: C, 55.76; H, 3.82; N, 1.62.

#### Example 331

- The above synthesis was followed using [(2,6-i-PrPh)<sub>2</sub>DABH<sub>2</sub>]PdMeCl (509 mg, 0.954 mmol), NaBAF (845 mg, 0.953 mmol), and t-BuA (154 μL, 1.1 equiv). The reaction mixture was stirred for 1 day and yielded an orange powder (1.24 g, 87.3%) that was composed of a mixture of 6a(t-Bu) (50%), 5'a(t-Bu) (42%), and 5a(t-Bu) (8%), according to <sup>1</sup>H NMR spectroscopy. 6a(t-Bu): <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz, rt) δ 8.27 and 8.25 (N=C(H)-C'(H)=N), 7.45 - 7.20 (m, 6, Haryl), 3.20 and 3.11 (septet, 2 each, J = 6.9, CHMe<sub>2</sub> and C'HMe<sub>2</sub>), 2.42 (t, 2, J = 5.9, CH<sub>2</sub>C(O)), 1.77 (t, 2, J = 5.3, PdCH<sub>2</sub>),

1.39, 1.36, 1.22 and 1.21 (d, 6 each,  $J = 6.7$ , CHMeMe' and C'HMeMe'), 1.01 (s, 9, OCMe<sub>3</sub>), 0.68 (pentet, 2,  $J = 6.1$ , PdCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C(O)); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100 MHz, rt, excluding Ar resonances)  $\delta$  182.6 (C(O)), 88.8 (OCMe<sub>3</sub>), 37.8, 33.6 and 23.9 (PdCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C(O)), 29.3 and 29.0 (CHMe<sub>2</sub>, C'HMe<sub>2</sub>), 27.8 (OCMe<sub>3</sub>), 24.8, 24.5, 22.7 and 22.6 (CHMeMe', C'HMeMe'); IR (CH<sub>2</sub>Cl<sub>2</sub>) 1615 cm<sup>-1</sup> [ $\nu$ (C(O))]; 5'a(t-Bu): <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz, rt; excluding Ar and i-Pr resonances)  $\delta$  8.29 and 8.22 (s, 1 each, N=C(H)-C'(H)=N), 2.53 (q, 1,  $J = 7.3$ , C(H)(Me)C(O)), 1.75 (d, 1,  $J = 8.9$ , PdCHH'), 1.53 (dd, 1,  $J = 9.0, 7.0$ , PdCHH'), 1.16 (OCMe<sub>3</sub>); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100 MHz, rt; excluding Ar resonances)  $\delta$  194.0 (C(O)), 90.6 (OCMe<sub>3</sub>), 45.9 (CHMeC(O)), 30.0 (PdCH<sub>2</sub>), 29.4, 29.3, 29.1 and 29.1 (CHMe<sub>2</sub>, C'HMe<sub>2</sub>, C''HMe<sub>2</sub>, C'''HMe<sub>2</sub>), 27.7 (OCMe<sub>3</sub>), 24.6, 24.4, 23.81, 23.79, 23.3, 23.3, 22.62 and 22.58 (CHMeMe', C'HMeMe', C''HMeMe', C'''HMeMe'), 18.7 (CHMeC(O)); IR (CH<sub>2</sub>Cl<sub>2</sub>) 1577 cm<sup>-1</sup> [ $\nu$ (C(O))]. 5a(t-Bu): <sup>1</sup>H NMR (vide infra); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100 MHz, rt)  $\delta$  190.4 (C(O)), 166.7 and 160.7 (N=C-C'=N), 48.1 (CH<sub>2</sub>C(O)), 35.3 (PdCHMe). Anal. Calcd for (C<sub>66</sub>H<sub>63</sub>BF<sub>24</sub>N<sub>2</sub>O<sub>2</sub>Pd): C, 53.22; H, 4.26; N, 1.88. Found: C, 53.55; H, 4.20; N, 1.59.

#### 25 Example 332

The above synthesis using [(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>]PdMeCl (499 mg, 0.889 mmol), NaBAF (786 mg, 0.887 mmol), and t-BuA (145  $\mu$ L, 1.1 equiv) was followed. The reaction mixture was stirred for 1 day to yield an orange powder (1.24 g, 91.8%) that consisted of a mixture of 6b(t-Bu) (26%), 5'b(t-Bu) (63%), and 5b(t-Bu) (11%), according to <sup>1</sup>H NMR spectroscopy. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 MHz, rt; diagnostic resonances only) 6b(t-Bu):  $\delta$  2.35 (t, 2,  $J = 6.1$ , CH<sub>2</sub>C(O)), 0.97 (s, 9, OCMe<sub>3</sub>), 0.60 (pentet, 2,  $J = 5.7$ , PdCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C(O)); 5'b(t-Bu):  $\delta$  2.43 (q, 1,  $J = 7.2$ , CHMeC(O)), 1.08 (s, 9, OCMe<sub>3</sub>); 5b(t-Bu):  $\delta$  0.99 (s, 9, OCMe<sub>3</sub>), 0.29 (d, 3,  $J = 6.74$ , PdCHMe); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>,

75 MHz, rt; diagnostic resonances only) **6b(t-Bu)**:  $\delta$  182.3 (C(O)), 88.3 (OCMe<sub>3</sub>), 37.9 and 31.9 (PdCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C(O)), 27.9 (OCMe<sub>3</sub>), 22.0 and 20.1 (N=C(Me)-C'(Me)=N); **5'b(t-Bu)**:  $\delta$  193.8 (C(O)), 178.8 and 171.8 (N=C-C'=N), 90.0 (OCMe<sub>3</sub>), 45.8 (CHMeC(O)), 28.7 (PdCH<sub>2</sub>), 21.1 and 19.6 (N=C(Me)-C'(Me)=N), 18.6 (CHMeC(O)); **5b(t-Bu)**  $\delta$  190.7 (C(O)), 48.4 (CH<sub>2</sub>C(O)), 33.9 (PdCHMe). Anal. Calcd for (C<sub>68</sub>H<sub>67</sub>BF<sub>24</sub>N<sub>2</sub>O<sub>2</sub>Pd): C, 53.82; H, 4.45; N, 1.85. Found: C, 53.62; H, 4.32; N, 1.55.

#### Example 333

The above synthesis was followed using [(2,6-i-Pr-Ph)<sub>2</sub>DABAn]PdMeCl (503 mg, 0.765 mmol), NaBAF (687 mg, 0.765 mmol), and t-BuA (125  $\mu$ L, 1.1 equiv). The reaction mixture was stirred for 1 day to yield an orange powder (1.08 g, 87.8%) that consisted of a mixture of **6c(t-Bu)** (47%), **5'c(t-Bu)** (50%), and **5c(t-Bu)** (3%), according to <sup>1</sup>H NMR spectroscopy. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 MHz, rt; diagnostic chelate resonances only) **6c(t-Bu)**:  $\delta$  2.48 (t, 2, J = 6.05, CH<sub>2</sub>C(O)), 1.80 (t, 2, PdCH<sub>2</sub>), 1.07 (s, 9, OCMe<sub>3</sub>), 0.73 (pentet, 2, J = 5.87, PdCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C(O)); **5'c(t-Bu)**:  $\delta$  2.57 (q, 1, J = 6.96, CHMeC(O)), 1.58 (dd, 1, J = 8.80, 6.96, PdCHH'), 1.21 (s, 9, OCMe<sub>3</sub>); **5c(t-Bu)**:  $\delta$  0.73 (d, 3, PdCHMe); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 75 MHz, rt; diagnostic chelate resonances only) **6c(t-Bu)**:  $\delta$  181.8 (C(O)), 87.9 (OCMe<sub>3</sub>), 37.4 and 32.2 (PdCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C(O)), 27.4 (OCMe<sub>3</sub>); **5'c(t-Bu)**:  $\delta$  193.0 (C(O)), 89.5 (OCMe<sub>3</sub>), 45.5 (CHMeC(O)), 28.5 (PdCH<sub>2</sub>), 27.2 (OCMe<sub>3</sub>), 18.1 (CHMeC(O)). Anal. Calcd for (C<sub>76</sub>H<sub>67</sub>BF<sub>24</sub>N<sub>2</sub>O<sub>2</sub>Pd): C, 56.57; H, 4.19; N, 1.74. Found: C, 56.63; H, 4.06; N, 1.52.

#### Example 334

The above synthesis using [(2,6-i-PrPh)<sub>2</sub>DABH<sub>2</sub>]PdMeCl (601 mg, 1.13 mmol), NaBAF (998 mg, 1.13 mmol), and FOA (337  $\mu$ L, 1.1 equiv) yielded after 1 day of stirring 1.21 g (59.2%) of **6a(FOA)** as a red foam: <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 MHz, 0  $^{\circ}$ C)  $\delta$  8.33 and 8.27

(s, 1 each,  $\text{N}=\text{C}(\text{H})-\text{C}'(\text{H})=\text{N}$ ), 7.4 - 7.2 (m, 6, Haryl), 3.85 (t, 2,  $\text{J}_{\text{HF}} = 13.05$ ,  $\text{OCH}_2(\text{CF}_2)_6\text{CF}_3$ ), 3.13 and 3.08 (septet, 2 each,  $\text{J} = 6.9$ ,  $\text{CHMe}_2$  and  $\text{C}'\text{HMe}_2$ ), 2.65 (t, 2,  $\text{J} = 5.62$ ,  $\text{CH}_2\text{C}(\text{O})$ ), 1.74 (t, 2,  $\text{J} = 5.59$ ,  $\text{PdCH}_2$ ), 1.36, 1.29, 1.15 and 1.13 (d, 6 each,  $\text{J} = 6.73 - 6.82$ ,  $\text{CHMeMe}'$ ,  $\text{C}'\text{HMeMe}'$ ), 0.76 (pentet, 2,  $\text{J} = 5.44$ ,  $\text{PdCH}_2\text{CH}_2\text{CH}_2\text{C}(\text{O})$ ).

#### Example 335

The above synthesis using [(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>]PdMeCl (637 mg, 1.13 mmol), NaBAF (1.00 g, 1.13 mmol), and FOA (339  $\mu\text{L}$ , 1.1 equiv) yielded after 1 day of stirring 1.36 g (65.2%) of 6b(FOA) as a yellow foam: <sup>1</sup>H NMR ( $\text{CD}_2\text{Cl}_2$ , 300 MHz, 0  $^\circ\text{C}$ )  $\delta$  7.5 - 7.0 (m, 6, Haryl), 3.64 (t, 2,  $\text{J}_{\text{HF}} = 12.72$ ,  $\text{OCH}_2(\text{CF}_2)_6\text{CF}_3$ ), 2.90 and 2.88 (septet, 2,  $\text{J} = 6.74$ ,  $\text{CHMe}_2$  and  $\text{C}'\text{HMe}_2$ ), 2.56 (t, 2,  $\text{J} = 5.82$ ,  $\text{CH}_2\text{C}(\text{O})$ ), 2.32 and 2.22 ( $\text{N}=\text{C}(\text{Me})-\text{C}'(\text{Me})=\text{N}$ ), 1.34, 1.27, 1.23 and 1.19 (d, 6 each,  $\text{J} = 6.75 - 6.82$ ,  $\text{CHMeMe}'$ ,  $\text{C}'\text{HMeMe}'$ ), 0.68 (pentet, 2,  $\text{J} = 5.83$ ,  $\text{PdCH}_2\text{CH}_2\text{CH}_2\text{C}(\text{O})$ ).

#### Examples 336-338

The labeling scheme given in Examples 328-335 is also used here. Spectral data for the BAF counterion is the same as given in Examples 328-335.

Low-Temperature NMR Observation of Methyl Acrylate Olefin Complex Formation and Chelate Formation and Rearrangement. One equivalent of MA was added to an NMR tube containing a 0.0198 M solution of [(2,6-iPrPh)<sub>2</sub>DABH<sub>2</sub>]PdMe(OEt<sub>2</sub>)]BAF in  $\text{CD}_2\text{Cl}_2$  (700  $\mu\text{L}$ ) at  $-78^\circ\text{C}$ , and the tube was transferred to the precooled NMR probe. After 14.25 min at  $-80^\circ\text{C}$ , approximately 80% of the ether adduct had been converted to the olefin complex. Two sets of bound olefin resonances were observed in a 86:14 ratio. This observation is consistent with the existence of two different rotamers of the olefin complex. Insertion of MA into the Pd-Me bond occurred with predominantly 2,1 regiochemistry to give the 4-membered chelate 4a(Me) at  $-80^\circ\text{C}$  ( $t_{1/2} \sim 2.0$  h). The resonances for the major rotamer of the olefin

complex disappeared before those of the minor rotamer. Much slower conversion of 4a(Me) to the 5-membered chelate 5a(Me) also began at -80°C. Upon warming to -60°C, complete and selective formation of 5a(Me) occurred in less than 4 h. The 5-membered chelate was relatively stable at temperatures below -50°C, however, upon warming to -20°C, rearrangement to the 6-membered chelate 6a(Me) was observed. NMR spectral data for the olefin complex, 4a(Me), and 5a(Me) follow. Spectral data for 6a(Me) is identical to that of the isolated chelate complex (see Examples 328-335).

Example 336

$\{[(2,6\text{-}i\text{-PrPh})_2\text{DABH}_2]\text{Pd}(\text{Me})[\text{H}_2\text{C}=\text{CHC}(\text{O})\text{OMe}]\}$ BAF.  
<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, -80°C, 400 MHz) Major Rotamer: δ 8.45 and 8.32 (s, 1 each, N=C(H)-C'(H)=N), 7.5 - 7.1 (m, 6, Haryl), 5.14 (d, J = 15.2, HH'C=), 4.96 (dd, J = 14.9, 8.6, =CHC(O)), 4.63 (d, J = 8.5, HH'C=), 3.68 (s, 3, OMe), 3.03, 2.90, 2.80 and 2.67 (septet, 1 each, CHMe<sub>2</sub>, C'HMe<sub>2</sub>, C''HMe<sub>2</sub>, C'''HMe<sub>2</sub>), 1.5 - 1.0 (doublets, 24, CHMe<sub>2</sub>), 0.61 (s, 3, PdMe); Minor Rotamer: δ 8.25 and 8.18 (s, 1 each, N=C(H)-C'(H)=N), 5.25 (d, 1, HH'C=), 4.78 (dd, 1, =CHC(O)), 4.58 (d, 1, HH'C=), 3.63 (OMe).

Example 337

$\{[(2,6\text{-}i\text{-PrPh})_2\text{DABH}_2]\text{Pd}[\text{CHEtC}(\text{O})\text{OMe}]\}$ BAF 4a(Me).  
<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz, -60°C) δ 8.25 and 8.22 (N=C(H)-C'(H)=N), 7.5 - 7.2 (m, 6, Haryl), 3.74 (s, 3, OMe), 3.55, 3.27, 3.08 and 2.76 (m, 1 each, CHMe<sub>2</sub>, C'HMe<sub>2</sub>, C''HMe<sub>2</sub>, C'''HMe<sub>2</sub>), 2.62 (dd, J = 10.8, 2.9, CHEt), 1.4 - 1.0 (doublets, 24, CHMe<sub>2</sub>), 0.79 and -0.49 (m, 1 each, CH(CHH'Me)), 0.71 (t, 3, J = 6.6, CH(CHH'Me)).

Example 338

$\{[(2,6\text{-}i\text{-PrPh})_2\text{DABH}_2]\text{Pd}[\text{CHMeCH}_2\text{C}(\text{O})\text{OMe}]\}$ BAF 5a(Me).  
<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz, -60°C) δ 8.24 and 8.21 (N=C(H)-C'(H)=N), 7.4 - 7.2 (m, 6, Haryl), 3.59 (s, 3, OMe), 3.47, 3.32, 2.98 and 2.81 (septet, 1 each, CHMe<sub>2</sub>, C'HMe<sub>2</sub>, C''HMe<sub>2</sub>, C'''HMe<sub>2</sub>), 3.08 (dd, 1, J = 18.4, 7.3, CHH'C(O)), 1.74 (pentet, 1, J = 6.9,

PdCHMe), 1.60 (d, 1,  $J = 18.6$ , CHH'C(O)), 1.34 (d, 6,  $J = 5.6$ , C'HMeMe' and C''HMeMe'), 1.32 (d, 3,  $J = 6.2$ , CHMeMe'), 1.24 (d, 3,  $J = 6.8$ , C'HMeMe'), 1.18 (d, 6,  $J = 6.8$ , C'HMeMe' and C''HMeMe'), 1.15 (d, 3,  $J = 6.8$ , C''HMeMe'), 1.08 (d, 3, CHMeMe'), 0.35 (d, 3,  $J = 6.9$ , PdCHMe);  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 100 MHz,  $-80^\circ\text{C}$ )  $\delta$  190.5 (C(O)), 166.1 ( $J_{\text{CH}} = 181$ ,  $\text{N}=\text{C}(\text{H})$ ), 160.7 ( $J_{\text{CH}} = 181$ ,  $\text{N}=\text{C}'(\text{H})$ ), 142.8 and 141.6 (Ar, Ar': Cipso), 139.0, 138.6, 138.2 and 137.7 (Ar: Co, Co' and Ar': Co, Co'), 128.8 and 128.2 (Ar, Ar': Cp), 124.1, 123.54, 123.48, 123.4 (Ar: Cm, Cm' and Ar': Cm, Cm'), 55.5 (OMe), 45.1 (CH<sub>2</sub>C(O)), 35.6 (PdCHMe), 28.8, 28.5, 28.1 and 27.8 (CHMe<sub>2</sub>, C'HMe<sub>2</sub>, C''HMe<sub>2</sub>, C'''HMe<sub>2</sub>), 25.6, 24.2, 23.1, 23.0, 22.7, 22.3, 21.9, 21.3, and 21.3 (CHMeMe', C'HMeMe', C''HMeMe' and PdCHMe).

#### Example 339-342

The labeling scheme given in Examples 328-335 is also used for Examples 339-342. Spectral data for the BAF counterion is the same as given in Examples 328-335.

Low-Temperature NMR Observation of *t*-Butyl Acrylate Olefin Complex Formation and Chelate Formation and Rearrangement. One equiv of *t*-BuA was added to an NMR tube containing a 0.0323 M solution of  $\{[(2,6\text{-i-PrPh})_2\text{DABH}_2]\text{PdMe}(\text{OEt}_2)\}\text{BAF}$  in  $\text{CD}_2\text{Cl}_2$  (700  $\mu\text{L}$ ) at  $-78^\circ\text{C}$ , and the tube was transferred to the precooled NMR probe. The olefin complex was observed at  $-80^\circ\text{C}$ , and the probe was then warmed to  $-70^\circ\text{C}$ . After 1 h at  $-70^\circ\text{C}$ , conversion to 5a(*t*-Bu) and 5'a(*t*-Bu) was almost complete, with small amounts (<10%) of the olefin complex and 4a(*t*-Bu) still present. Conversion of 5a(*t*-Bu) to 6a(*t*-Bu) was followed at  $-10^\circ\text{C}$  ( $t_{1/2}$ -1 h). When this experiment was repeated using 5 equiv of *t*-BuA, conversion to 5a, 5'a and 6a was observed at  $-80^\circ\text{C}$ . After allowing the solution to stand at rt for 5 days, partial conversion to the unsubstituted 5-membered chelate 5''a(*t*-Bu) was observed. Spectral data for the olefin complex, 4a(*t*-Bu), 5a(*t*-Bu) and

5''a(t-Bu) follow. Spectral data for 5'a(t-Bu) and 6a(t-Bu) are identical to that of the isolated chelate complexes (see Examples 328-335).

Example 339

- 5         $\{[(2,6\text{-i-PrPh})_2\text{DABH}_2]\text{PdMe}[\text{H}_2\text{C}=\text{CHC}(\text{O})\text{O-t-Bu}]\}$ BAF.  
 $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 400 MHz,  $-80^\circ\text{C}$ )  $\delta$  8.45 and 8.30 (s, 1 each  $\text{N}=\text{C}(\text{H})-\text{C}'(\text{H})=\text{N}$ ), 7.4 - 7.2 (m, 6, Haryl), 5.15 (d, 1,  $J = 15.3$ ,  $\text{HH}'\text{C}=\text{CHC}(\text{O})$ ), 4.89 (dd, 1,  $J = 14.7$ , 8.4, and 2.64 (septets, 1 each,  $\text{CHMe}_2$ ,  $\text{C}'\text{HMe}_2$ ),  $\text{C}''\text{HMe}_2$  and  $\text{C}''' \text{HMe}_2$ ), 1.31 (s, 9,  $\text{OCMe}_3$ ), 1.5 - 0.8 (doublets, 24,  $\text{CHMe}_2$ ), 0.60 (s, 3,  $\text{PdMe}$ ).

Example 340

- 15         $\{[(2,6\text{-i-PrPh})_2\text{DABH}_2]\text{Pd}[\text{CHEtC}(\text{O})\text{O-t-Bu}]\}$ BAF 4a(t-Bu).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 400 MHz,  $-70^\circ\text{C}$ )  $\delta$  8.22 and 8.21 (s, 1 each,  $\text{N}=\text{C}(\text{H})-\text{C}'(\text{H})=\text{N}$ ), 2.21 (d, 1,  $J = 9.2$ ,  $\text{PdCHEt}$ ), 0.71 (t, 3,  $J = 7.9$ ,  $\text{PdCH}(\text{CH}_2\text{Me})$ ), 0.5 and -0.4 (br m, 1 each,  $\text{PdCH}(\text{CHH}'\text{Me})$ ).

Example 341

- 20         $\{[(2,6\text{-i-PrPh})_2\text{DABH}_2]\text{Pd}[\text{CHMeCH}_2\text{C}(\text{O})\text{O-t-Bu}]\}$ BAF 5a(t-Bu).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 400 MHz,  $-40^\circ\text{C}$ )  $\delta$  8.28 and 8.24 (s, 1 each,  $\text{N}=\text{C}(\text{H})-\text{C}'(\text{H})=\text{N}$ ), 7.4 - 7.2 (m, 6, Haryl), 3.44, 3.32, 2.96 and 2.86 (septet, 1 each,  $\text{CHMe}_2$ ,  $\text{C}'\text{HMe}_2$ ,  $\text{C}''\text{HMe}_2$ ,  $\text{C}''' \text{HMe}_2$ ), 2.94 (dd, 1,  $J = 18.6$ , 7.1,  $\text{CHH}'\text{C}(\text{O})$ ), 1.79 (pentet, 1,  $J = 6.7$ ,  $\text{PdCHMe}$ ), 1.62 (d, 1,  $J = 18.5$ ,  $\text{CHH}'\text{C}(\text{O})$ ), 1.4 - 1.0 (doublets, 24,  $\text{CHMe}_2$ ), 1.10 (s, 9,  $\text{OCMe}_3$ ), 0.22 (d, 3,  $J = 6.9$ ,  $\text{PdCHMe}$ ).

Example 342

- 30         $\{[(2,6\text{-i-PrPh})_2\text{DABH}_2]\text{Pd}[\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{O-t-Bu}]\}$ BAF 5''a(t-Bu).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 400 MHz, rt)  $\delta$  2.40 (t, 2,  $J = 7.0$ ,  $\text{CH}_2\text{C}(\text{O})$ ), 1.65 (t, 2,  $J = 7.0$ ,  $\text{PdCH}_2$ ).

Example 343

- 35        The labeling scheme given in Examples 328-335 is also used for Example 343. Spectral data for the BAF counterion is the same as given in Examples 328-335.

Low-Temperature NMR Observation of FOA Chelate Formation and Rearrangement. One equiv of FOA was

added to an NMR tube containing a 0.0285 M solution of  
{[(2,6-i-PrPh)<sub>2</sub>DABH<sub>2</sub>]PdMe(OEt<sub>2</sub>)}BAF (1a) at -78°C in  
CD<sub>2</sub>Cl<sub>2</sub> (700 µL), and the tube was briefly shaken at  
this temperature. A <sup>1</sup>H NMR spectrum at -80°C showed  
5 that FOA was not dissolved. The sample was allowed to  
warm slightly as it was shaken again and another  
spectrum was then acquired at -80°C. Approximately  
equal amounts of 5a(FOA) and 6a(FOA) were observed  
along with small amounts of the ether adduct 1a and FOA  
10 (an olefin complex was not observed). Rearrangement of  
5a(FOA) to 6a(FOA) was observed at -40°C and was  
complete upon warming to -30°C. NMR spectral data for  
5a(FOA) follow. Spectral data for 6a(FOA) are  
identical with that of the isolated complex (vide  
15 supra).

{[(2,6-i-  
PrPh)<sub>2</sub>DABH<sub>2</sub>]Pd[CHMeCH<sub>2</sub>C(O)OCH<sub>2</sub>(CF<sub>2</sub>)<sub>6</sub>CF<sub>3</sub>]}BAF 5a(FOA).  
<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 MHz, -40°C) δ 8.23 and 8.22 (s, 1  
each, N=C(H)-C'(H)=N), 3.47 (t, 2, J<sub>HF</sub> = 13.38,  
20 OCH<sub>2</sub>(CF<sub>2</sub>)<sub>6</sub>CF<sub>3</sub>), 3.20 (dd, 1, J = 19.25, 7.28,  
CHH'C(O)), 2.58 (pentet, 1, J = 6.99, PdCHMe), 1.77 (d,  
1, J = 19.81, CHH'C(O)), 0.33 (d, 3, J = 6.88, PdCHMe).  
Spectral data for the BAF counterion is the same as  
given in Examples 328-335.

25 Example 344

NMR Observation of {[(2,6-i-  
PrPh)<sub>2</sub>DABH<sub>2</sub>]Pd[CHR'CH<sub>2</sub>CH<sub>2</sub>C(O)OMe]}BAF and {[(2,6-i-  
PrPh)<sub>2</sub>DABH<sub>2</sub>]Pd[CH<sub>2</sub>CH<sub>2</sub>C(O)OMe]}BAF. A solution of  
{[(2,6-i-PrPh)<sub>2</sub>DABH<sub>2</sub>]PdMe(OEt<sub>2</sub>)}BAF (21.5 mg, 0.0150  
30 mmol) in 700 µL of CD<sub>2</sub>Cl<sub>2</sub> was prepared at -78°C.  
Ethylene (5 equiv) was added via gastight syringe and  
the tube was shaken briefly to dissolve the ethylene.  
Methyl acrylate (5 equiv) was then added to the  
solution, also via gastight microliter syringe, and the  
35 tube was shaken briefly again. The tube was  
transferred to the NMR probe, which was precooled to -  
80°C. Resonances consistent with the formation of the  
ethylene adduct {[(2,6-i-PrPh)<sub>2</sub>DABH<sub>2</sub>]PdMe(H<sub>2</sub>C=CH<sub>2</sub>)}BAF



were observed. The solution was warmed and ethylene insertion was monitored at -40 to -20°C. The consumption of one equiv of methyl acrylate occurred as the last equiv of ethylene disappeared, and resonances consistent with the formation of a substituted 6-membered chelate complex  $\{[(2,6\text{-i-PrPh})_2\text{DABH}_2]\text{Pd}[\text{CHR}'\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OMe}]\}\text{BAF}$  were observed [8.30 and 8.29 ( $\text{N}=\text{C}(\text{H})-\text{C}'(\text{H})=\text{N}$ ), 3.17 (OMe)]. The large upfield shift of the methoxy resonance is particularly diagnostic for formation of the 6-membered chelate complex in these systems. The substituted 6-membered chelate complex was observed at -20°C and initially upon warming to RT. After 2 h at RT, decomposition of the substituted 6-membered chelate complex had begun. After 24 h at RT, an additional 0.5 equiv of MA had been consumed and triplets at 2.42 and 1.66 ppm, consistent with the formation of the unsubstituted 5-membered chelate complex  $\{[(2,6\text{-i-PrPh})_2\text{DABH}_2]\text{Pd}[\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OMe}]\}\text{BAF}$ , were observed. Spectral data for the BAF counterion is the same as given in Examples 328-335.

#### Example 345

NMR Observation of  $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{Pd}(\text{CHR}'\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OMe})\}\text{BAF}$ . The procedure of Example 344 was followed with analogous results, e.g., resonances for the formation of a substituted 6-membered chelate complex  $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{Pd}(\text{CHR}'\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OMe})\}\text{BAF}$  were observed following complete ethylene consumption [3.03 (s, OMe), 3.12, 2.96, 2.89, 2.83 (septets,  $\text{CHMe}_2$ ,  $\text{C}'\text{HMe}_2$ ,  $\text{C}''\text{HMe}_2$  and  $\text{C}''' \text{HMe}_2$ ), 2.23 and 2.19 (s,  $\text{N}=\text{C}(\text{Me})-\text{C}'(\text{Me})=\text{N}$ )]. Again, the large upfield shift of the methoxy resonance is diagnostic for the formation of the six-membered chelate complex. The observation of four i-propyl methine resonances (vs. two i-propyl methine resonances in the unsubstituted six-membered chelate complex) reflects the asymmetry introduced in the molecule due to the introduction of the R' substituent on  $\text{C}_\alpha$  of the

chelate ring and further supports the proposed structure. Spectral data for the BAF counterion is the same as given in Examples 328-335.

Example 346

5           {[(2,6-i-  
PrPh)<sub>2</sub>DABH<sub>2</sub>]Pd(H<sub>2</sub>C=CH<sub>2</sub>)[CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C(O)OMe]}BAF.  
Ethylene was transferred at -78°C via gastight  
microliter syringe to an NMR tube containing a CD<sub>2</sub>Cl<sub>2</sub>  
solution of the chelate complex {[(2,6-i-  
10 PrPh)<sub>2</sub>DABH<sub>2</sub>]Pd[CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C(O)OMe]}BAF. NMR data for the  
ethylene complex follow; it was observed in equilibrium  
with the starting chelate complex: <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300  
MHz, 182°K) δ 8.30 and 8.29 (s, 1 each, N=C(H)-  
C'(H)=N), 7.38 - 7.24 (m, 6, H<sub>aryl</sub>), 3.72 (s, 3, OMe),  
15 3.43 (br s, 4, H<sub>2</sub>C=CH<sub>2</sub>), 3.10 (m, 2, CHMe<sub>2</sub>), 2.70 (m,  
2, C'HMe<sub>2</sub>), 2.20 (m, 2, CH<sub>2</sub>C(O)), 1.25, 1.16, 1.09 and  
1.07 (d, 6 each, J = 7, CHMeMe', C'HMeMe'), 1.20 (PdCH<sub>2</sub>  
(obscured by CHMeMe' peaks, observed by H,H-COSY)),  
0.56 (m, 2, PdCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C(O)); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz,  
20 -80°C) δ 178.9 (C(O)), 162.7 (J<sub>CH</sub> = 179, N=C), 162.5  
(J<sub>CH</sub> = 179, N=C'), 141.3 and 140.5 (Ar, Ar': Cipso),  
138.5 and 138.1 (Ar, Ar': C<sub>O</sub>), 128.5 and 128.3 (Ar,  
Ar': C<sub>p</sub>), 124.1 and 124.0 (Ar, Ar': C<sub>O</sub>), 122.9 (J<sub>CH</sub> =  
159.3, free H<sub>2</sub>C=CH<sub>2</sub>), 70.2 (J<sub>CH</sub> = 158.6, bound  
25 H<sub>2</sub>C=CH<sub>2</sub>), 53.0 (OMe), 36.5, 33.0 and 22.6  
(PdCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C(O)), 27.8 (CHMe<sub>2</sub>, C'HMe<sub>2</sub>), 25.6, 25.3,  
22.1 and 21.4 (CHMeMe', C'HMeMe'). Spectral data for  
the BAF counterion is the same as given in Examples  
328-335.

Example 347

30           {[(2,6-i-  
PrPh)<sub>2</sub>DABMe<sub>2</sub>]Pd(H<sub>2</sub>C=CH<sub>2</sub>)[(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C(O)OMe]}BAF.  
Ethylene was transferred at -78°C via gastight  
microliter syringe to an NMR tube containing a CD<sub>2</sub>Cl<sub>2</sub>  
35 solution of the chelate complex {[(2,6-i-  
PrPh)<sub>2</sub>DABMe<sub>2</sub>]Pd[CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C(O)OMe]}BAF. NMR data for  
the ethylene complex follow; even at low temperature  
and in the presence of a large excess of ethylene, this

complex could only be observed in the presence of at least an equimolar amount of the corresponding six-membered chelate:  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ , 300 MHz, 172°K):  $\delta$  7.35 - 7.19 (m, 6, H<sub>aryl</sub>), 4.31 (br s, 4, H<sub>2</sub>C=CH<sub>2</sub>), 3.45 (s, 3, OMe), 2.73 - 2.54 (m, 4, CHMe<sub>2</sub>), 2.38 and 2.22 (s, 3 each, N=C(Me)-C'(Me)=N), 1.64 (m, 2, CH<sub>2</sub>C(O)), 1.02 (d, 6, J = 6, CHMeMe'). From the available H,H-COSY data, the remaining PdCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C(O)- and CHMe-signals could not be unambiguously assigned, due to the presence of the six-membered chelate. Spectral data for the BAF counterion is the same as given in Examples 328-335.

Example 348

{[(2,6-i-PrPh)<sub>2</sub>DABAn]Pd(H<sub>2</sub>C=CH<sub>2</sub>)[CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C(O)OMe]}BAF.  
Ethylene was transferred at -78°C via gastight microliter syringe to an NMR tube containing a CD<sub>2</sub>Cl<sub>2</sub> solution of the chelate complex {[(2,6-i-PrPh)<sub>2</sub>DABAn]Pd(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C(O)OMe)}BAF. NMR data for the ethylene complex follow; it was observed in equilibrium with the starting chelate complex:  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ , 300 MHz, 178°K):  $\delta$  8.06 and 8.02 (d, J = 8, 1 each, An and An': H<sub>p</sub> and H'<sub>p</sub>), 7.50 - 7.38 (m, 8, An and An': H'<sub>m</sub> and H<sub>m</sub>, Ar: H<sub>m</sub> and H'<sub>p</sub>), 6.48 (d, J = 7, 2, An and An': H<sub>o</sub> and H'<sub>o</sub>), 4.56 (br s, 4, H<sub>2</sub>C=CH<sub>2</sub>), 3.45 (s, 3, OMe), 2.99 and 2.91 (m, 2 each, CHMe<sub>2</sub> and C'CHMe<sub>2</sub>), 1.77 (m, 2, CH<sub>2</sub>C(O)), 1.29, 1.27, 0.82 and 0.77 (d, J = 6 - 7, 6 each, CHMeMe', C'CHMeMe'). H,H-COSY reveals that the remaining PdCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C(O)-signals are obscured by the CHMe-signals at 1.2 ppm. Spectral data for the BAF counterion is the same as given in Examples 328-335.

Example 349

{[(2,6-i-PrPh)<sub>2</sub>DABH<sub>2</sub>]Pd[CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C(O)OCH<sub>2</sub>(CF<sub>2</sub>)<sub>6</sub>CF<sub>3</sub>](H<sub>2</sub>C=CH<sub>2</sub>)}BAF  
Ethylene (0.78 equiv) was added via gastight microliter syringe to a 0.0105 M solution of the chelate complex {[(2,6-i-PrPh)<sub>2</sub>DABH<sub>2</sub>]Pd[CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C(O)OCH<sub>2</sub>(CF<sub>2</sub>)<sub>6</sub>CF<sub>3</sub>]}BAF in

CD<sub>2</sub>Cl<sub>2</sub> (700 μL). NMR data for the ethylene complex follow; it was observed in equilibrium with the starting chelate complex: <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 MHz, 213.0°K) δ 8.40 and 8.25 (N=C(H)-C'(H)=N), 7.5 - 7.1 (m, 6, H<sub>aryl</sub>), 4.50 (t, 2, J<sub>HF</sub> = 13.39, OCH<sub>2</sub>(CF<sub>2</sub>)<sub>6</sub>CF<sub>3</sub>), 4.41 (s, 4, H<sub>2</sub>C=CH<sub>2</sub>), 2.94 and 2.70 (septet, 2 each, CHMe<sub>2</sub>, C'HMe<sub>2</sub>), 1.80 (t, 3, CH<sub>2</sub>C(O)), 1.4 - 1.0 (CHMeMe', C'HMeMe', PdCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C(O)). Spectral data for the BAF counterion is the same as given in Examples 328-335.

#### Example 350

A 12 mg (0.02 mmol) sample of [(2,6-i-PrPh)<sub>2</sub>DABAn]NiBr<sub>2</sub> was placed in a 25 mL high pressure cell. The reactor was purged with argon. The reactor was cooled to 0°C before 2 mL of a 10 % MAO solution in toluene was added under a positive argon purge. The reactor was filled (3/4 full) with liquid CO<sub>2</sub> (4.5 MPa) and a 689 kPa head pressure of ethylene was added by continuous flow. A 6 degree exotherm was observed. A layer of polyethylene formed immediately at the ethylene CO<sub>2</sub> interface. After 20 minutes, the cell was vented and the polyethylene removed from the reactor. The polymer was dried in vacuo for several hours. Polyethylene (2.05 g) was isolated; M<sub>n</sub> = 597,000, M<sub>w</sub>/M<sub>n</sub> = 2.29, T<sub>m</sub> = 128°C. This example demonstrates the applicability of liquid CO<sub>2</sub> as a solvent for polymerization in these catalyst systems.

#### Example 351

A 12 mg (0.02 mmol) sample of [(2,6-i-PrPh)<sub>2</sub>DABAn]NiBr<sub>2</sub> was placed in a 25 mL high pressure cell and the reactor was purged with argon. The reactor was heated to 40°C and 2 mL of a 10 % MAO solution in toluene was added. CO<sub>2</sub> (20.7 MPa) and ethylene (3.5 MPa, continuous flow) was then added to the reactor. Polyethylene began adhering to the sapphire window within minutes. After 20 minutes, the cell was vented and the polyethylene removed from the reactor. The polymer was dried in vacuo for several

hours. Polyethylene (0.95 g) was isolated;  $M_n = 249,000$ ,  $M_w/M_n = 2.69$ ,  $T_m = 113^\circ\text{C}$ . This example demonstrates the applicability of supercritical  $\text{CO}_2$  as a solvent for polymerization in these catalyst systems.

5

Example 352

A standard solution of  $[(2,6\text{-}i\text{-PrPh})_2\text{DABAN}]\text{NiBr}_2$  was prepared as follows: 1,2-difluorobenzene (10 mL) was added to 6.0 mg of  $[(2,6\text{-}i\text{-PrPh})_2\text{DABAN}]\text{NiBr}_2$  ( $8.4 \times 10^{-6}$  mol) in a 10 mL volumetric flask. The standard solution was transferred to a Kontes flask and stored under an argon atmosphere.

10 A 1000 mL Parr® stirred autoclave under an argon atmosphere, was charged with 1 mL of a standard solution of  $[(2,6\text{-}i\text{-PrPh})_2\text{DABAN}]\text{NiBr}_2$  ( $8.3 \times 10^{-7}$  mol), and 200 mL of dry, deaerated toluene. The reactor was purged with ethylene before addition of 2 mL of a 10% MAO solution in toluene. The autoclave was rapidly pressurized with ethylene to 1.4 MPa as the internal temperature increased from  $25^\circ\text{C}$  to  $45^\circ\text{C}$  within seconds.

20 Activation of the internal cooling system returned the reactor temperature to  $30^\circ\text{C}$ . After 10 minutes, the ethylene was vented and acetone and water were added to quench the reaction. Solid polyethylene was recovered from the reactor collected and washed with 6 M HCl,  $\text{H}_2\text{O}$ , and acetone. The resulting polymer was dried under high vacuum overnight to yield 7.0 g ( $1.8 \times 10^6$  TO/h) of polyethylene. Differential scanning calorimetry:  $T_m = 118^\circ\text{C}$  (133 J/g). Gel permeation chromatography (trichlorobenzene,  $135^\circ\text{C}$ , polystyrene reference, results calculated as polyethylene using universal calibration theory):  $M_n = 470,000$ ;  $M_w = 1,008,000$ ;  $M_w/M_n = 2.14$ .  $^{13}\text{C}$ -NMR analysis: total methyls/1000  $\text{CH}_2$  (27.6), methyl (21.7), ethyl (2.6), propyl (.7), butyl (1), amyl (.4).

35

Example 353

A 1000 mL Parr® stirred autoclave under an argon atmosphere, was charged with 1 mL of a standard solution of  $[(2,6\text{-}i\text{-PrPh})_2\text{DABAN}]\text{NiBr}_2$  ( $8.3 \times 10^{-7}$  mol),

and 200 mL of dry, deaerated toluene. The reactor was purged with ethylene before addition of 2 mL of a 10% MAO solution in toluene. The autoclave was rapidly pressurized with ethylene to 2.8 MPa as the internal temperature increased from 25°C to 48°C within seconds. Activation of the internal cooling system returned the reactor temperature to -30°C. After 10 minutes, the ethylene was vented and acetone and water were added to quench the reaction. Solid polyethylene was recovered from the reactor collected and washed with 6 M HCl, H<sub>2</sub>O, and acetone. The resulting polymer was dried under high vacuum overnight to yield 8.85 g (2.3x10<sup>6</sup> TO/h) of polyethylene. DSC: T<sub>m</sub> = 122°C. GPC (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal calibration theory): M<sub>n</sub> = 485,000; M<sub>w</sub> = 1,042,000; M<sub>w</sub>/M<sub>n</sub> = 2.15. <sup>13</sup>C-NMR analysis: total methyls/1000 CH<sub>2</sub> (21.3), methyl (16.3), ethyl (2.1), propyl (0.7), butyl (0.9), amyl (0.2).

#### Example 354

A 1000 mL Parr® stirred autoclave under an argon atmosphere, was charged with 1 mL of a standard solution of [(2,6-*i*-PrPh)<sub>2</sub>DABAn]NiBr<sub>2</sub> (8.3x10<sup>-7</sup> mol), and 200 mL of dry, deaerated toluene. The reactor was purged with ethylene before addition of 2 mL of a 10% MAO solution in toluene. The autoclave was rapidly pressurized with ethylene to 4.1 MPa as the internal temperature increased from 25°C to 45°C within seconds. Activation of the internal cooling system returned the reactor temperature to -30°C. After 10 min, the ethylene was vented and acetone and water were added to quench the reaction. Solid polyethylene was recovered from the reactor collected and washed with 6 M HCl, H<sub>2</sub>O, and acetone. The resulting polymer was dried under high vacuum overnight to yield 7.45 g (1.9x10<sup>6</sup> TO/h) of polyethylene. DSC: T<sub>m</sub> = 126°C. GPC (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal

calibration theory):  $M_n = 510,000$ ;  $M_w = 1,109,000$ ;  $M_w/M_n = 2.17$ .  $^{13}\text{C}$ -NMR analysis: total methyls/1000  $\text{CH}_2$  (5.1), methyl (5.1), ethyl (0), propyl (0), butyl (0), amyl (0).

5

Example 355

A 1 mg ( $1.7 \times 10^{-6}$  mol) sample of [(2,6-i-PrPh) $_2$ DABH $_2$ ]NiBr $_2$  was placed in a Parr $^{\circledR}$  1000 mL stirred autoclave under argon. The autoclave was sealed and 200 mL of dry toluene was added. The reactor was purged with ethylene before addition of 1.5 mL of a 10% MAO solution in toluene. The autoclave was rapidly pressurized with ethylene to 1.4 MPa as the internal temperature increased from 25°C to 45°C within seconds. Activation of the internal cooling system returned the reactor temperature to -30°C. After 10 min, the ethylene was vented and acetone and water were added to quench the reaction. Solid polyethylene was recovered from the reactor collected and washed with 6 M HCl, H $_2$ O, and acetone. The resulting polymer was dried under high vacuum overnight to yield 14.1 g ( $1.8 \times 10^6$  TO/h) of polyethylene. DSC:  $T_m = 126^\circ\text{C}$  (151 J/g). GPC (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal calibration theory):  $M_n = 32,000$ ;  $M_w = 89,000$ ;  $M_w/M_n = 2.75$ .

25

Example 356

A 1 mg ( $1.7 \times 10^{-6}$  mol) sample of [(2,6-i-PrPh) $_2$ DABH $_2$ ]NiBr $_2$  was placed in a Parr $^{\circledR}$  1000 mL stirred autoclave under argon. The autoclave was sealed and 200 mL of dry toluene was added. The reactor was purged with ethylene before addition of 1.5 mL of a 10% MAO solution in toluene. The autoclave was rapidly pressurized with ethylene to 2.1 MPa as the internal temperature increased from 25°C to 50°C within seconds. Activation of the internal cooling system returned the reactor temperature to -30°C. After 10 min, the ethylene was vented and acetone and water were added to quench the reaction. Solid polyethylene was

35

recovered from the reactor collected and washed with 8 M HCl, H<sub>2</sub>O, and acetone. The resulting polymer was dried under high vacuum overnight to yield 16.1 g (2x10<sup>6</sup> TO/h) of polyethylene. DSC: T<sub>m</sub> = 129°C (175 J/g). GPC (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal calibration theory): M<sub>n</sub> = 40,000; M<sub>w</sub> = 89,000; M<sub>w</sub>/M<sub>n</sub> = 2.22.

#### Example 357

10 A 1.2 mg (1.9x10<sup>-6</sup> mol) sample of [(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>]NiBr<sub>2</sub> was placed in a Parr® 1000 mL stirred autoclave under argon. The autoclave was sealed and 200 mL of dry toluene was added. The reactor was purged with ethylene before addition of 2.0  
15 mL of a 10% MAO solution in toluene. The autoclave was rapidly pressurized with ethylene to 1.4 MPa as the internal temperature increased from 24°C to 31°C within seconds. Activation of the internal cooling system returned the reactor temperature to -25°C. After 12  
20 min, the ethylene was vented and acetone and water were added to quench the reaction. Solid polyethylene was recovered from the reactor collected and washed with 6 M HCl, H<sub>2</sub>O, and acetone. The resulting polymer was dried under high vacuum overnight to yield 8 g (9x10<sup>5</sup>  
25 TO/h) of polyethylene. DSC: Broad melt beginning approximately 0°C with a maximum at 81°C (25 J/g). GPC (trichlorobenzene, 135 °C, polystyrene reference, results calculated as polyethylene using universal calibration theory): M<sub>n</sub> = 468,000; M<sub>w</sub> = 1,300,000;  
30 M<sub>w</sub>/M<sub>n</sub> = 2.81. <sup>13</sup>C-NMR analysis: total methyls/1000 CH<sub>2</sub> (46.6), methyl (37.0), ethyl (2.4), propyl (1.6), butyl (1.3), amyl (1.4).

#### Example 358

35 A 1.2 mg (1.9x10<sup>-6</sup> mol) sample of [(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>]NiBr<sub>2</sub> was placed in a Parr® 1000 mL stirred autoclave under argon. The autoclave was sealed and 200 mL of dry toluene was added. The reactor was purged with ethylene before addition of 2.0



mL of a 10% MAO solution in toluene. The autoclave was rapidly pressurized with ethylene to 2.8 MPa as the internal temperature increased from 24°C to 34°C within seconds. After 12 min, the ethylene was vented and acetone and water were added to quench the reaction. Solid polyethylene was recovered from the reactor collected and washed with 6 M HCl, H<sub>2</sub>O, and acetone. The resulting polymer was dried under high vacuum overnight to yield 6.5 g (6x10<sup>5</sup> TO/h) of polyethylene.

10 DSC: Broad melt beginning approximately 60°C with a maximum at 109°C (80 J/g). GPC (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal calibration theory):  $M_n = 616,000$ ;  $M_w = 1,500,000$ ;  $M_w/M_n = 2.52$ . <sup>13</sup>C-NMR

15 analysis: total methyls/1000 CH<sub>2</sub> (32.0), methyl (24.6), ethyl (2.6), propyl (1.3), butyl (0.6), amyl (1.3).

#### Example 359

A 1.2 mg (1.9x10<sup>-6</sup> mol) sample of [(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>]NiBr<sub>2</sub> was placed in a Parr® 1000 mL stirred autoclave under argon. The autoclave was sealed and 200 mL of dry toluene was added. The reactor was purged with ethylene before addition of 2.0 mL of a 10% MAO solution in toluene. The autoclave was

25 rapidly pressurized with ethylene to 4.1 MPa. After 12 min, the ethylene was vented and acetone and water were added to quench the reaction. Solid polyethylene was recovered from the reactor collected and washed with 6 M HCl, H<sub>2</sub>O, and acetone. The resulting polymer was

30 dried under high vacuum overnight to yield 7.2 g (7x10<sup>5</sup> TO/h) of polyethylene. GPC (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal calibration theory):  $M_n = 800,000$ ;  $M_w = 1,900,000$ ;  $M_w/M_n = 2.43$ . <sup>13</sup>C-NMR

35 analysis: total methyls/1000 CH<sub>2</sub> (18.7), methyl (14.9), ethyl (1.7), propyl (1.1), butyl (0.3), amyl (0.4).

#### Example 360

A 1.5 mg ( $2.4 \times 10^{-6}$  mol) sample of [(2,6-*i*-PrPh)<sub>2</sub>DABMe<sub>2</sub>]NiBr<sub>2</sub> and 200 mL of dry toluene was added to a Parr® 1000 mL stirred autoclave under an argon atmosphere. The reactor was heated to 50°C and purged with ethylene before addition of 3.0 mL of a 7% MMAO solution in heptane. The autoclave was rapidly pressurized with ethylene to 690 kPa. After 10 min, the ethylene was vented and acetone and water were added to quench the reaction. Solid polyethylene was recovered from the reactor collected and washed with 6 M HCl, H<sub>2</sub>O, and acetone. The resulting polymer was dried under high vacuum overnight to yield 6.25 g ( $6 \times 10^5$  TO/h) of polyethylene. DSC: Broad melt beginning approximately -25°C with a maximum at 50°C; T<sub>g</sub> = -36°C. GPC (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal calibration theory): M<sub>n</sub> = 260,000; M<sub>w</sub> = 736,000; M<sub>w</sub>/M<sub>n</sub> = 2.83.

#### Example 361

A 1.5 mg ( $2.4 \times 10^{-6}$  mol) sample of [(2,6-*i*-PrPh)<sub>2</sub>DABMe<sub>2</sub>]NiBr<sub>2</sub> and 200 mL of dry toluene was added to a Parr® 1000 mL stirred autoclave under an argon atmosphere. The reactor was heated to 65°C and purged with ethylene before addition of 3.0 mL of a 7% MMAO solution in heptane. The autoclave was rapidly pressurized with ethylene to 690 kPa. After 10 min, the ethylene was vented and acetone and water were added to quench the reaction. Solid polyethylene was recovered from the reactor collected and washed with 6 M HCl, H<sub>2</sub>O, and acetone. The resulting polymer was dried under high vacuum overnight to yield 7.6 g ( $7 \times 10^5$  TO/h) of polyethylene. DSC: Broad melt beginning approximately -50°C with a maximum at 24°C. GPC (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal calibration theory): M<sub>n</sub> = 176,000; M<sub>w</sub> = 438,000; M<sub>w</sub>/M<sub>n</sub> = 2.49.

#### Example 362

A 1.5 mg ( $2.4 \times 10^{-6}$  mol) sample of [(2,6-*i*-PrPh)<sub>2</sub>DABMe<sub>2</sub>]NiBr<sub>2</sub> and 200 mL of dry toluene was added to a Parr® 1000 mL stirred autoclave under an argon atmosphere. The reactor was heated to 80°C and purged with ethylene before addition of 3.0 mL of a 7% MMAO solution in heptane. The autoclave was rapidly pressurized with ethylene to 690 kPa. After 10 min, the ethylene was vented and acetone and water were added to quench the reaction. Solid polyethylene was recovered from the reactor collected and washed with 6 M HCl, H<sub>2</sub>O, and acetone. The resulting polymer was dried under high vacuum overnight to yield 1.0 g ( $0.9 \times 10^5$  TO/h) of polyethylene. DSC: Broad melt beginning approximately -50°C with a maximum at -12°C. GPC (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal calibration theory):  $M_n = 153,000$ ;  $M_w = 273,000$ ;  $M_w/M_n = 1.79$ .

Example 363

A 1.5 mg ( $2.4 \times 10^{-6}$  mol) sample of [(2,6-*i*-PrPh)<sub>2</sub>DABMe<sub>2</sub>]NiBr<sub>2</sub> and 200 mL of dry toluene was added to a Parr® 1000 mL stirred autoclave under an argon atmosphere. The reactor was heated to 80°C and purged with ethylene before addition of 3.0 mL of a 7% MMAO solution in heptane. The autoclave was rapidly pressurized with ethylene to 2.1 MPa. After 10 min, the ethylene was vented and acetone and water were added to quench the reaction. Solid polyethylene was recovered from the reactor collected and washed with 6 M HCl, H<sub>2</sub>O, and acetone. The resulting polymer was dried under high vacuum overnight to yield 1.05 g ( $0.9 \times 10^5$  TO/h) of polyethylene. DSC: Broad melt beginning approximately -25°C with a maximum at 36°C.

Example 364

A standard solution of [(2,6-*i*-PrPh)<sub>2</sub>DABAn]NiBr<sub>2</sub> was prepared as follows: 1,2-difluorobenzene (10 mL) was added to 6.0 mg of [(2,6-*i*-PrPh)<sub>2</sub>DABAn]NiBr<sub>2</sub> ( $8.4 \times 10^{-6}$  mol) in a 10 mL volumetric flask. The

standard solution was transferred to a Kontes flask and stored under an argon atmosphere.

A 250 mL Schlenk flask was charged with 1 mL of a standard solution of  $[(2,6-i\text{-PrPh})_2\text{DABAn}] \text{NiBr}_2$  ( $8.3 \times 10^{-7}$  mol), and 100 mL of dry, deaerated toluene. The flask was cooled to  $-20^\circ\text{C}$  in a dry ice isopropanol bath and filled with ethylene (100 kPa, absolute) before addition of 1.5 mL of a 10% MAO solution in toluene. After 30 min, acetone and water were added to quench the reaction. Solid polyethylene was recovered from the flask collected and washed with 6 M HCl,  $\text{H}_2\text{O}$ , and acetone. The resulting polymer was dried under high vacuum overnight to yield 0.8 g ( $7 \times 10^4$  TO/h) of polyethylene. GPC (trichlorobenzene,  $135^\circ\text{C}$ , polystyrene reference, results calculated as polyethylene using universal calibration theory):  $M_n = 519,000$ ;  $M_w = 768,000$ ;  $M_w/M_n = 1.48$ .

#### Example 365

A 250 mL Schlenk flask was charged with 20 mg of  $[(2,6-i\text{-PrPh})_2\text{DABMe}_2] \text{NiBr}_2$  ( $3.2 \times 10^{-5}$  mol), and 75 mL of dry, deaerated toluene. The flask was cooled to  $0^\circ\text{C}$  filled with propylene (100 kPa absolute) before addition of 1.5 mL of a 10% MAO solution in toluene. After 30 min, acetone and water were added to quench the reaction. Solid polypropylene was recovered from the flask and washed with 6 M HCl,  $\text{H}_2\text{O}$ , and acetone. The resulting polymer was dried under high vacuum overnight to yield 0.15 g polypropylene. DSC:  $T_g = -31^\circ\text{C}$ . GPC (trichlorobenzene,  $135^\circ\text{C}$ , polystyrene reference):  $M_n = 25,000$ ;  $M_w = 37,000$ ;  $M_w/M_n = 1.47$ .

#### Example 366

Cyclopentene (16  $\mu\text{L}$ , 10 eq) was added to a suspension of  $[(2,6-i\text{-PrPh})_2\text{DABAn}] \text{NiBr}_2$  (12 mg,  $1.6 \times 10^{-5}$  mol) in 50 mL of dry toluene. A 10% MAO solution (1.5 mL) in toluene was added and the homogenous mixture stirred for 2 h at  $25^\circ\text{C}$ . After 2 h, the flask was filled with ethylene (100 kPa, absolute) and the reaction stirred for 15 min. Acetone and water were

added to quench the polymerization and precipitate the polymer. Solid polyethylene was recovered from the flask collected and washed with 6 M HCl, H<sub>2</sub>O, and acetone. The resulting polymer was dried under high vacuum overnight to yield 3.6 g (32,000 TO/h) polyethylene. GPC: (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal calibration theory):  $M_n = 87,000$ ;  $M_w = 189,000$ ;  $M_w/M_n = 2.16$ . A control experiment was run under identical conditions to that described above except no cyclopentene was added to stabilize the activated nickel complex. Polyethylene (380 mg, 3500 TO/h) was isolated. This example demonstrates the applicability of the Ni agostic cation as a potential soluble stable initiator for the polymerization of ethylene and other olefin monomers.

#### Example 367

1-Hexene (3 mL, 6 vol %) was added to a suspension of [(2,6-*i*-PrPh)<sub>2</sub>DABAN]NiBr<sub>2</sub> (12 mg,  $1.6 \times 10^{-5}$  mol) in 50 mL of dry toluene. The flask was cooled to -20°C in a dry ice isopropanol bath and 1.5 mL of a 10% MAO solution in toluene was added. After stirring the reaction for 1.5 h, acetone and water were added to quench the polymerization and precipitate the polymer. Solid poly(1-hexene) was recovered from the flask collected and washed with 6 M HCl, H<sub>2</sub>O, and acetone. The resulting polymer was dried under high vacuum overnight to yield 200 mg poly(1-hexene). GPC (trichlorobenzene, 135°C, polystyrene reference):  $M_n = 44,000$ ;  $M_w = 48,000$ ;  $M_w/M_n = 1.09$ .

#### Example 368

1-Hexene (2.5 mL, 6 vol %) was added to a suspension of [(2,6-*i*-PrPh)<sub>2</sub>DABAN]NiBr<sub>2</sub> (6 mg,  $8.3 \times 10^{-6}$  mol) in 50 mL of dry toluene. The flask was cooled to -10°C in a dry ice isopropanol bath and 1.5 mL of a 7% MMAO solution in heptane was added. After stirring the reaction for 1 h, acetone and water were added to quench the polymerization and precipitate the polymer.

Solid poly(1-hexene) was recovered from the flask and washed with 6 M HCl, H<sub>2</sub>O, and acetone. The resulting polymer was dried under high vacuum overnight to yield 250 mg poly(1-hexene). GPC (dichloromethane, polystyrene reference):  $M_n = 51,000$ ;  $M_w = 54,000$ ;  $M_w/M_n = 1.06$ .

#### Example 369

Propylene (1 atm) was added to a Schlenk flask charged with a suspension of [(2,6-*i*-PrPh)<sub>2</sub>DABAN]NiBr<sub>2</sub> (12 mg,  $1.7 \times 10^{-5}$  mol) in 50 mL of dry toluene after cooling the mixture to -15°C in a dry ice isopropanol bath. A 7% MMAO solution in heptane was added. After stirring the reaction for 30 min, acetone and water were added to quench the polymerization and precipitate the polymer. Solid polypropylene was recovered from the flask and washed with 6 M HCl, H<sub>2</sub>O, and acetone. The resulting polymer was dried under high vacuum overnight to yield 800 mg polypropylene. GPC (dichloromethane, polystyrene reference):  $M_n = 84,000$ ;  $M_w = 96,000$ ;  $M_w/M_n = 1.14$ .

#### Example 370

Propylene (100 kPa, absolute) was added to a Schlenk flask charged with a suspension of [(2,6-*i*-PrPh)<sub>2</sub>DABAN]NiBr<sub>2</sub> (12 mg,  $1.7 \times 10^{-5}$  mol) in 50 mL of dry toluene. After cooling the mixture to -15°C in a dry ice isopropanol bath, a 7% MMAO solution in heptane was added. After stirring the reaction for 30 min, 5 mL of dry 1-hexene was added and the propylene removed in vacuo. The polymerization was allowed to stir for an additional 30 min before acetone and water were added to quench the polymerization and precipitate the polymer. Solid polypropylene-*b*-poly(1-hexene) was recovered from the flask and washed with 6 M HCl, H<sub>2</sub>O, and acetone. The resulting polymer was dried under high vacuum overnight to yield 1.8 g polypropylene-*b*-poly(1-hexene). GPC (dichloromethane, polystyrene reference):  $M_n = 142,000$ ;  $M_w = 165,000$ ;  $M_w/M_n = 1.16$ . <sup>1</sup>H-NMR analysis: indicates the presence of both a

polypropylene and poly(1-hexene) block.  $^1\text{H}$ -NMR also suggests that the DP of the propylene block is substantially higher than the DP of the 1-hexene block. DSC analysis:  $T_g = -18^\circ\text{C}$  corresponding to the  
5 polypropylene block. No other transitions were observed.

#### Example 371

1-Octadecene (4 mL, 8 vol %) was added to a suspension of  $[(2,6\text{-i-PrPh})_2\text{DABAN}]\text{NiBr}_2$  (12 mg,  $1.6 \times 10^{-5}$  mol) in 50 mL of dry toluene. The flask was cooled  
10 to  $-10^\circ\text{C}$  in a dry ice isopropanol bath and 2 mL of a 7% MMAO solution in heptane was added. After stirring the reaction for 1 h, acetone and water were added to quench the polymerization and precipitate the polymer.  
15 Solid poly(1-octadecene) was recovered from the flask collected and washed with 6 M HCl,  $\text{H}_2\text{O}$ , and acetone. The resulting polymer was dried under high vacuum overnight to yield 200 mg poly(1-octadecene). GPC (trichlorobenzene,  $135^\circ\text{C}$ , polystyrene reference):  $M_n =$   
20 19,300;  $M_w = 22,700$ ;  $M_w/M_n = 1.16$ . DSC:  $T_m = 37^\circ\text{C}$ .  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ) analysis 47 branches/1000 C (theoretical 56 branches/1000 C).

#### Example 372

A 12-mg (.022 mmol) sample of  $[(\text{para-Me-Ph})_2\text{DABMe}_2]\text{NiBr}_2$  was placed in a Parr® 1000 mL stirred  
25 autoclave under an argon atmosphere with 200 mL of dry toluene (reactor temperature was  $65^\circ\text{C}$ ). The reactor was purged with ethylene and 1.5 mL (100 eq) of a 10% MAO solution in toluene was added to the suspension.  
30 The autoclave was rapidly pressurized to 5.5 MPa and the reaction was stirred for 60 min. A  $15^\circ\text{C}$  exotherm was observed. The oligomerization was quenched upon addition of acetone and water. The solvent was removed in vacuo resulting in 20 g of ethylene oligomers.  $^1\text{H}$ -  
35 NMR ( $\text{CDCl}_3$ ) analysis 83%  $\alpha$ -olefin.

#### Example 373

A 12-mg (.022 mmol) sample of  $[\text{Ph}_2\text{DABAN}]\text{NiBr}_2$  was placed in a Parr® 1000 mL stirred autoclave under an

argon atmosphere with 200 mL of dry toluene (reactor temperature was 55°C). The reactor was purged with ethylene and 2 mL (100 eq) of a 7% MMAO solution in heptane was added to the suspension. The autoclave was rapidly pressurized to 5.5 MPa and the reaction was stirred for 60 minutes. A 18°C exotherm was observed. The oligomerization was quenched upon addition of acetone and water. The solvent was removed in vacuo resulting in 26 g (corrected for loss of C<sub>4</sub>, C<sub>6</sub>, and C<sub>8</sub> during work-up) of ethylene oligomers. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) and GC analysis: Distribution: C<sub>4</sub>-C<sub>18</sub>, C<sub>4</sub> = 6.0%, C<sub>6</sub> = 21%, C<sub>8</sub> = 22%, C<sub>10</sub> = 17%, C<sub>12</sub> = 16%, C<sub>14</sub> = 13%, C<sub>16</sub> = 5%, C<sub>18</sub> = trace; 90% α-olefin.

#### Example 374

A 12-mg (.022 mmol) sample of [Ph<sub>2</sub>DABAn]NiBr<sub>2</sub> was placed in a Parr® 1000 mL stirred autoclave under an argon atmosphere with 200 mL of dry toluene (reactor temperature was 45°C). The reactor was purged with ethylene and 2 mL (100 eq) of a 7% MMAO solution in heptane was added to the suspension. The autoclave was rapidly pressurized to 5.5 MPa and the reaction was stirred for 60 min. The oligomerization was quenched upon addition of acetone and water. The solvent was removed in vacuo resulting in 32 g (corrected for loss of C<sub>4</sub>, C<sub>6</sub>, and C<sub>8</sub> during work-up) of ethylene oligomers. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) and GC analysis: Distribution: C<sub>4</sub>-C<sub>20</sub>, C<sub>4</sub> = 9.0%, C<sub>6</sub> = 19%, C<sub>8</sub> = 19%, C<sub>10</sub> = 15%, C<sub>12</sub> = 14%, C<sub>14</sub> = 11%, C<sub>16</sub> = 5%, C<sub>18</sub> = 4%, C<sub>20</sub> = 2%; 92% α-olefin.

#### Example 375

A 12-mg (.022 mmol) sample of [(Ph)DABAn]NiBr<sub>2</sub> was placed in a 1000 mL stirred autoclave under an argon atmosphere with 200 mL of deaerated toluene (reactor temperature was 25°C). The reactor was purged with ethylene and 2 mL (100 eq) of a 10% MAO solution in toluene was added to the suspension. The autoclave was rapidly pressurized to 2.1 MPa and the reaction was stirred for 30 min. A 20°C exotherm was observed. The



oligomerization was quenched upon addition of acetone and water. The solvent was removed in vacuo resulting in 16.1g of a fluid/waxy mixture (50,000 TO/h based on isolated oligomer).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) analysis 80%  $\alpha$ -olefin. Distribution of isolated oligomers by GC analysis:  $\text{C}_{10}$  = 20%,  $\text{C}_{12}$  = 28%,  $\text{C}_{14}$  = 23%,  $\text{C}_{16}$  = 15%,  $\text{C}_{18}$  = 10%,  $\text{C}_{20}$  = 4%. All  $\text{C}_4$ ,  $\text{C}_6$ ,  $\text{C}_8$  and some  $\text{C}_{10}$  was lost during work-up.

#### Example 376

10 A 12-mg (.022 mmol) sample of  $[(\text{Ph})\text{DABAN}]\text{NiBr}_2$  was placed in a 1000 mL stirred autoclave under an argon atmosphere with 200 mL of deaerated toluene (reactor temperature was 25°C). The reactor was purged with ethylene and 2 mL (100 eq) of a 10% MAO solution in  
15 toluene was added to the suspension. The autoclave was rapidly pressurized to 4.1 MPa and the reaction was stirred for 60 minutes. A 20°C exotherm was observed. The oligomerization was quenched upon addition of acetone and water. The solvent was removed in vacuo  
20 resulting in 28.3g of crude product (50,000 TO/h based on isolated oligomer). Trace Al was removed by an aqueous/organic work-up of the crude mixture.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) analysis 85%  $\alpha$ -olefin. Distribution of isolated oligomers by GC analysis:  $\text{C}_{10}$  = 13%,  $\text{C}_{12}$  =  
25 30%,  $\text{C}_{14}$  = 26%,  $\text{C}_{16}$  = 18%,  $\text{C}_{18}$  = 10%,  $\text{C}_{20}$  = 3%. All  $\text{C}_4$ ,  $\text{C}_6$ ,  $\text{C}_8$  and some  $\text{C}_{10}$  was lost during work -up.

#### Example 377

A 12-mg (.022 mmol) sample of  $[(\text{Ph})\text{DABAN}]\text{NiBr}_2$  was placed in a 1000 mL stirred autoclave under an argon  
30 atmosphere with 200 mL of deaerated toluene (reactor temperature was 25°C). The reactor was purged with ethylene and 2 mL (100 eq) of a 10% MAO solution in toluene was added to the suspension. The autoclave was rapidly pressurized to 6.7 MPa and the reaction was  
35 stirred for 60 min. A 15°C exotherm was observed. The oligomerization was quenched upon addition of acetone and water. The solvent was removed in vacuo resulting in 21.6g of crude product (40,000 TO/h based on

isolated oligomer).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) analysis 93%  $\alpha$ -olefin. Distribution of isolated oligomers by GC analysis:  $\text{C}_{10}$  = 13%,  $\text{C}_{12}$  = 27%,  $\text{C}_{14}$  = 26%,  $\text{C}_{16}$  = 18%,  $\text{C}_{18}$  = 12%,  $\text{C}_{20}$  = 5%. All  $\text{C}_4$ ,  $\text{C}_6$ ,  $\text{C}_8$  and some  $\text{C}_{10}$  was  
5 lost during work-up.

#### Example 378

A 12-mg (.022 mmol) sample of  $[\text{Ph}_2\text{DABAn}]\text{NiBr}_2$  was placed in a 1000 mL stirred autoclave under an argon atmosphere with 200 mL of dry toluene (reactor  
10 temperature was  $50^\circ\text{C}$ ). The reactor was purged with ethylene and 2 mL (100 eq) of a 10% MAO solution in toluene was added to the suspension. The autoclave was rapidly pressurized to 5.5 MPa and the reaction was stirred for 60 minutes. A  $15^\circ\text{C}$  exotherm was observed.  
15 The oligomerization was quenched upon addition of acetone and water. The solvent was removed in vacuo resulting in 22.3g of crude product (40,000 TO/h based on isolated oligomer).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) analysis 92%  $\alpha$ -olefin. Distribution of isolated oligomers by GC  
20 analysis:  $\text{C}_{10}$  = 10%,  $\text{C}_{12}$  = 28%,  $\text{C}_{14}$  = 25%,  $\text{C}_{16}$  = 19%,  $\text{C}_{18}$  = 12%,  $\text{C}_{20}$  = 6%. All  $\text{C}_4$ ,  $\text{C}_6$ ,  $\text{C}_8$  and some  $\text{C}_{10}$  was lost during work-up.

#### Examples 379-393

##### General Procedure for Copolymerizations

25 (a) Experiments at Ambient Pressure: A Schlenk flask containing the catalyst precursor was cooled to  $-78^\circ\text{C}$ , evacuated, and placed under an ethylene atmosphere. In subsequent additions, methylene chloride and the acrylate were added to the cold flask  
30 via syringe. The solution was allowed to warm to room temperature and stirred with a magnetic stir bar. After the specified reaction time, the reaction mixture was added to ~600 mL of methanol in order to precipitate the polymer. Next, the methanol was  
35 decanted off of the polymer, which was then dissolved in ~600 mL of  $\text{Et}_2\text{O}$  or petroleum ether. (For copolymerizations with FOA, a second precipitation of the polymer solution into methanol was often necessary

in order to remove all of the acrylate from the polymer.) The solution was filtered through a plug of Celite® and/or neutral alumina, the solvent was removed, and the polymer was dried in vacuo for several days. The copolymers were isolated as clear, free-flowing or viscous oils. The copolymers were often darkened by traces of palladium black, which proved difficult to remove in some cases. Polymers with high FOA incorporation were white, presumably due to phase separation of the fluorinated and hydrocarbon segments.

(b) Experiments at Elevated Pressure: Reactions were carried out in a mechanically stirred 300 mL Parr® reactor, equipped with an electric heating mantle controlled by a thermocouple dipping into the reaction mixture. A solution of 0.1 mmol of catalyst precursor in methylene chloride, containing the functionalized comonomer (5-50 mL, total volume of the liquid phase: 100 mL), was transferred via cannula to the reactor under a nitrogen atmosphere. After repeatedly flushing with ethylene or propylene, constant pressure was applied by continuously feeding the gaseous olefin and the contents of the reactor were vigorously stirred. After the specified reaction time, the gas was vented. Volatiles were removed from the reaction mixture in vacuo, and the polymer was dried under vacuum overnight. In representative runs, the volatile fraction was analyzed by GC for low-molecular-weight products. Residual monomers (tBuA, FOA) or homooligomers of the functionalized comonomer (MVK) were removed by precipitating the polymer from methylene chloride solution with methanol. This procedure did not significantly alter the polymer composition.

Copolymer Spectral Data. In addition to the signals of the methyl, methylene and methine groups originating from ethylene or propylene, the <sup>1</sup>H and <sup>13</sup>C NMR spectra of the copolymers exhibit characteristic resonances due to the functionalized comonomer. The

IR-spectra display the carbonyl band of the functional groups originating from the comonomer.

Ethylene-MA Copolymer:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  3.64 (s,  $\text{OCH}_3$ ), 2.28 (t,  $J = 7$ ,  $\text{CH}_2\text{C}(\text{O})$ ), 1.58 (m,  $\text{CH}_2\text{CH}_2\text{C}(\text{O})$ );  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 100 MHz)  $\delta$  176 ( $\text{C}(\text{O})$ ), 50.9 ( $\text{OCH}_3$ ); IR (film):  $1744\text{ cm}^{-1}$  [ $\nu(\text{C}(\text{O}))$ ].

Ethylene-FOA Copolymer:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  4.58 (t,  $J_{\text{HF}} = 14$ ,  $\text{OCH}_2(\text{CF}_2)_6\text{CF}_3$ ), 2.40 (t,  $J = 7$ ,  $\text{CH}_2\text{C}(\text{O})$ ), 1.64 (m,  $\text{CH}_2\text{CH}_2\text{C}(\text{O})$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  172.1 ( $\text{C}(\text{O})$ ), 59.3 (t,  $J_{\text{CF}} = 27$ ,  $\text{OCH}_2(\text{CF}_2)_6\text{CF}_3$ ); IR (film):  $1767\text{ cm}^{-1}$  [ $\nu(\text{C}(\text{O}))$ ].

Ethylene-tBuA Copolymer:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  2.18 (t,  $J = 7$ ,  $\text{CH}_2\text{C}(\text{O})$ ), 1.55 (m,  $\text{CH}_2\text{CH}_2\text{C}(\text{O})$ ), 1.42 (s,  $\text{OCMe}_3$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 62 MHz)  $\delta$  173.4 ( $\text{C}(\text{O})$ ); IR (film):  $1734\text{ cm}^{-1}$  ( $\text{CO}$ ).

Ethylene-MVK Copolymer:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 250 MHz)  $\delta$  2.39 (t,  $J = 7$ ,  $\text{CH}_2\text{C}(\text{O})$ ), 2.11 (s,  $\text{C}(\text{O})\text{CH}_3$ ), 1.5 (m,  $\text{CH}_2\text{CH}_2\text{C}(\text{O})$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 62 MHz)  $\delta$  209 ( $\text{C}(\text{O})$ ); IR (film):  $1722\text{ cm}^{-1}$  [ $\nu(\text{C}(\text{O}))$ ].

Propylene-MA Copolymer:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 250 MHz)  $\delta$  3.64 (s,  $\text{OCH}_3$ ), 2.3 (m,  $\text{CH}_2\text{C}(\text{O})$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 62 MHz)  $\delta$  174.5 ( $\text{C}(\text{O})$ ), 51.4 ( $\text{OCH}_3$ ); IR (film):  $1747\text{ cm}^{-1}$  [ $\nu(\text{C}(\text{O}))$ ].

Propylene-FOA Copolymer:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 250 MHz)  $\delta$  4.57 (t,  $J_{\text{HF}} = 14$ ,  $\text{OCH}_2(\text{CF}_2)_6\text{CF}_3$ ), 2.39 (m,  $\text{CH}_2\text{C}(\text{O})$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 62 MHz)  $\delta$  172.2 ( $\text{C}(\text{O})$ ), 59.3 (t,  $J_{\text{CF}} = 27$ ,  $\text{OCH}_2(\text{CF}_2)_6\text{CF}_3$ ); IR (film):  $1767\text{ cm}^{-1}$  [ $\nu(\text{C}(\text{O}))$ ].

Results of the various polymerization are given in the Table below.

Ex.	react.		results				polymer	
	monomers	conc.	comon.	p(atm)	mass	comon.-	TONe	M <sub>n</sub> f
Ex.	cat.	comon.	p(atm)	polymer	incorp.	d E re. P	comon.	(x 10 <sup>-3</sup> ) M / M
379	6b	E / MA	0.6 M	2	22.2	1.0%	7710	78 88 1.8
380	6b	E / MA	2.9 M	2	4.3	6.1%	1296	84 26 1.6
381	6b	E / MA	5.8 M	2	1.8	12.1%	455	63 11 1.6
382	6b	E / MA	5.8 M	6	11.2	4.0%	3560	148 42 1.8
383	6a	E / MA	5.8 M	6	1.2	5.0%	355	19 0.39 -
384	6b	E / MA	5.8 M	6	1.2	4.7%	364	18 10 1.8
385	6b	E / tBuA	3.4 M	6	2.8	0.7%	956	7 25 1.6
386	6b	E / tBuA	0.4 M	1	1.9	0.4%	665	3 6 1.8
387	1a	E / FOA	0.6 M	1	1.5	0.3%	506	2 3 1.6
388	1b	E / FOA	0.6 M	1	27.5	0.6%	8928	55 106 3.1
389	6b	E / FOA	1.8	1	9.5	0.9%	2962	27 95 2.7
390	6b	E / MVK	3.0 M	6	1.8	1.3%	626	8 7 1.5
391	6b	E	-	6	10.3	-	37127	384 3.1
392	6b	P / MA	0.6 M	6	5.0	1.1%	1179	13 37 1.8
393	6b	P / FOA	1.8 M	2	1.0	5.6%	145	9 18 1.8

<sup>a</sup>0.1 mmol catalyst (Ex. 391: 0.01 mmol); solvent: CH<sub>2</sub>Cl<sub>2</sub> (total volume CH<sub>2</sub>Cl<sub>2</sub> and comonomer: 100 mL; Ex. 387 & 388: 60 mL) temperature: 35 °C (Ex. 386-389 & 391 °C); reaction time: 18.5 h (Ex. 386-388: 24 h; Ex. 389, 37 h); <sup>b</sup>Complexes 6: {[(2,6-i-PrPh)<sub>2</sub>DABR<sub>2</sub>]Pd[CH<sub>2</sub>CH<sub>2</sub>C(O)OMe]}BAP (6a); R = Me (6b); Complexes 1: {[(2,6-i-PrPh)<sub>2</sub>DABR<sub>2</sub>]Pd(Me)(OBt<sub>2</sub>)}BAP; R = H (1a); R = Me (1b); <sup>c</sup>Ethylene (E), propylene (P), methyl acrylate (MA), tert-butyl acrylate (tBuA), H<sub>2</sub>C=CHC(O)OCH<sub>2</sub>(CF<sub>2</sub>)<sub>6</sub>CF<sub>3</sub> (FOA), methyl vinyl ketone (MVK). <sup>d</sup>In mol %. <sup>e</sup>Turnover number = moles of substrate converted per mole of catalyst. <sup>f</sup>Determined by GPC vs. polystyrene standards; <sup>g</sup>Determined by <sup>1</sup>H NMR spectroscopy of the non-volatile product fraction; -0.5 g of volatile products formed additionally; <sup>h</sup>Branching: Ethylene Copolymers: -100 methyl groups/1000 carbon atoms (Tg's: -77 - -67 °C); Propylene Copolymers: -210 methyl groups/1000 carbon atoms.

Example 394

Et<sub>2</sub>O (30 mL) was added to a round bottom flask containing 445 mg (1.10 mmol) of (2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub> and 316 mg (1.15 mmol) of Ni(COD)<sub>2</sub>. Methyl acrylate  
 5 (100 µL) was then added to the flask via microliter syringe. The resulting blue solution was stirred for several hours before the Et<sub>2</sub>O was removed in vacuo. The compound was then dissolved in petroleum ether and the resulting solution was filtered and then cooled to  
 10 -35°C in the drybox freezer. Purple single crystals of [(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>]Ni[H<sub>2</sub>C=CHCO(OMe)] were isolated:  
<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 MHz, -40°C) δ 7.4 - 7.2 (m, 6, Haryl), 3.74 (br septet, 1, CHMe<sub>2</sub>), 3.09 (septet, 1, J = 6.75, C'HMe<sub>2</sub>), 2.93 (septet, 1, J = 6.75, C''HMe<sub>2</sub>),  
 15 2.85 (s, 3, OMe), 2.37 (br septet, 1, C'''HMe<sub>2</sub>), 2.10 (dd, 1, J = 13.49, 8.10, H<sub>2</sub>C=CHC(O)OMe), 1.66 (dd, 1, J = 13.49, 4.05, HH'C=CHC(O)OMe), 1.41 (d, 3, J = 6.75, CHMeMe'), 1.35 (dd, 1, J = 8.10, 4.05, HH'C=CHC(O)OMe),  
 1.26 (d, 3, J = 8.10, C'HMeMe'), 1.24 (d, 3, J = 8.09, C''HMeMe'),  
 20 C'''HMeMe'), 1.13 (d, 3, J = 6.75, C'HMeMe'), 1.09 - 1.03 (doublets, 12, CHMeMe', C'HMeMe', C'''HMeMe'), 0.79 and 0.62 (s, 3 each, N=C(Me)-C'(Me)=N); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 MHz, -20 °C) δ 174.2 (C(O)OMe), 166.6 and 165.5 (N=C-C'=N), 147.9 and 146.8 (Ar, Ar': Cipso),  
 25 139.5, 139.0, 138.2 and 137.7 (Ar: C<sub>O</sub>, C'<sub>O</sub> and Ar': C<sub>O</sub>, C'<sub>O</sub>), 125.6 and 125.4 (Ar, Ar': C<sub>p</sub>), 123.5, 123.4, 123.3 and 123.0 (Ar: C<sub>m</sub>, C'<sub>m</sub> and Ar': C<sub>m</sub>, C'<sub>m</sub>), 49.9 and 39.8 (H<sub>2</sub>C=CHC(O)OMe), 28.8, 28.5, 28.4 and 28.3 (CHMe<sub>2</sub>, C'HMe<sub>2</sub>, C''HMe<sub>2</sub>, C'''HMe<sub>2</sub>), 26.1  
 30 (H<sub>2</sub>C=CHC(O)OMe), 24.3, 23.8, 23.6, 23.4, 23.0, 22.9, 22.7 and 22.7 (CHMeMe', C'HMeMe', C''HMeMe', C'''HMeMe'), 20.21 and 20.16 (N=C(Me)-C'(Me)=N).

Example 395

In a nitrogen-filled drybox, 289 mg (0.525 mmol)  
 35 of [(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>Ni(H<sub>2</sub>C=CHCO(OMe))] and 532 mg (0.525 mmol) of H(OEt<sub>2</sub>)<sub>2</sub>BAF were placed together in a round bottom flask. The flask was cooled in the -35°C freezer before adding 20 mL of cold (-35°C) Et<sub>2</sub>O to it.

The reaction mixture was then allowed to warm to room temperature as it was stirred for 2 h. The solution was then filtered and the solvent was removed in vacuo to yield 594 mg (80.1%) of the 4-membered chelate,

5 {[(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>]Ni[CHMeC(O)OMe]}BAF, as a burnt orange powder: <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 MHz, rt) δ 7.72 (s, 8, BAF: H<sub>O</sub>), 7.56 (s, 4, BAF: H<sub>P</sub>), 7.5 - 7.2 (m, 6, H<sub>aryl</sub>), 3.52 (s, 3, OMe), 3.21 (q, 1, J = 6.75, CHMeC(O)OMe), 3.45, 3.24, 3.02 and 3.02 (septet, 1

10 each, CHMe<sub>2</sub>, C'HMe<sub>2</sub>, C''HMe<sub>2</sub> and C'''HMe<sub>2</sub>), 2.11 and 2.00 (s, 3 each, N=C(Me)-C'(Me)=N), 1.55, 1.50, 1.47, 1.33, 1.28, 1.24, 1.23 and 1.17 (d, 3 each, CHMeMe', C'HMeMe', C''HMeMe' and C'''HMeMe'), -0.63 (d, 3, J = 6.75, CHMeC(O)OMe); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 MHz, rt) δ

15 178.2, 177.0 and 174.1 (C(O)OMe, N=C-C'=N), 162.2 (q, JCB = 49.7, BAF: C<sub>ipso</sub>), 141.2 and 139.8 (Ar, Ar': C<sub>ipso</sub>), 139.4, 138.89, 138.79 and 138.40 (Ar, Ar': C<sub>O</sub>, C<sub>O'</sub>), 135.2 (BAF: C<sub>O</sub>), 130.0 and 129.6 (Ar, Ar': C<sub>p</sub>, C<sub>p'</sub>), 129.3 (q, BAF: C<sub>m</sub>), 125.6, 125.2, 125.0 and 124.7

20 (Ar, Ar': C<sub>m</sub>, C'<sub>m</sub>), 125.0 (q, JCF = 272.5, BAF: CF<sub>3</sub>), 117.9 (BAF: C<sub>p</sub>), 53.6 (OMe), 30.3, 30.0, 29.9 and 29.8 (CHMe<sub>2</sub>, C'HMe<sub>2</sub>, C''HMe<sub>2</sub>, C'''HMe<sub>2</sub>), 24.5, 24.1, 24.0, 23.7, 23.33, 23.26, 23.1 and 23.1 (CHMeMe', C'HMeMe', C''HMeMe', C'''HMeMe'), 20.6 and 19.5 (N=C-C'=N), 6.9

25 (CHMeC(O)OMe).

#### Examples 396-400

Polymerization of ethylene by {[(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>]Ni[CHMeC(O)OMe]}BAF. This compound was used to catalyze the polymerization of polyethylene at

30 temperatures between RT to 80°C. Addition of a Lewis acid often resulted in improved yields of polymer.

General Polymerization Procedure for Examples 396-400. In the drybox, a glass insert was loaded with {[(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>]Ni[CHMeC(O)OMe]}BAF. In

35 addition, 2 equiv of a Lewis acid (when used) was added to the insert. The insert was cooled to -35°C in a drybox freezer, 5 mL of deuterated solvent was added to the cold insert, and the insert was then capped and

sealed. Outside of the drybox, the cold tube was placed under 6.9 MPa of ethylene and allowed to warm to RT or 80°C as it was shaken mechanically for 18 h. An aliquot of the solution was used to acquire a  $^1\text{H}$  NMR spectrum. The remaining portion was added to -20 mL of MeOH in order to precipitate the polymer. The polyethylene was isolated and dried under vacuum.

Example 396

Polymerization Conditions:  $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{Ni}[\text{CHMeC}(\text{O})\text{OMe}]\}$ BAF (84.8 mg, 0.06 mmol); No Lewis Acid;  $\text{C}_6\text{D}_6$ ; RT. No polymer was isolated and polymer formation was not observed in the  $^1\text{H}$  NMR spectrum.

Example 397

Polymerization Conditions:  $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{Ni}[\text{CHMeC}(\text{O})\text{OMe}]\}$ BAF (84.8 mg, 0.06 mmol); 2 Equiv  $\text{BPh}_3$ ;  $\text{C}_6\text{D}_6$ , RT. Solid white polyethylene (0.91 g) was isolated.

Example 398

Polymerization Conditions:  $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{Ni}[\text{CHMeC}(\text{O})\text{OMe}]\}$ BAF (84.8 mg, 0.06 mmol); 2 Equiv  $\text{B}[3,5\text{-trifluoromethylphenyl}]_3$ ;  $\text{C}_6\text{D}_6$ , RT. Solid white polyethylene (0.89 g) was isolated.

Example 399

Polymerization Conditions:  $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{Ni}[\text{CHMeC}(\text{O})\text{OMe}]\}$ BAF; 2 Equiv  $\text{BPh}_3$ ;  $\text{C}_6\text{D}_6$ , 80°C. Polyethylene (4.3 g) was isolated as a spongy solid.

Example 400

Polymerization Conditions:  $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{Ni}[\text{CHMeC}(\text{O})\text{OMe}]\}$ BAF (84.8 mg, 0.06 mmol); No Lewis Acid;  $\text{CDCl}_3$ , 80°C. Polyethylene (2.7 g) was isolated as a spongy solid.

Example 401

An NMR tube was loaded with  $\{[(2,6\text{-i-PrPh})_2\text{DABH}_2]\text{NiMe}(\text{OEt}_2)\}$ BAF. The tube was capped with a septum, the septum was wrapped with Parafilm®, and the tube was cooled to -78°C.  $\text{CD}_2\text{Cl}_2$  (700  $\mu\text{L}$ ) and one



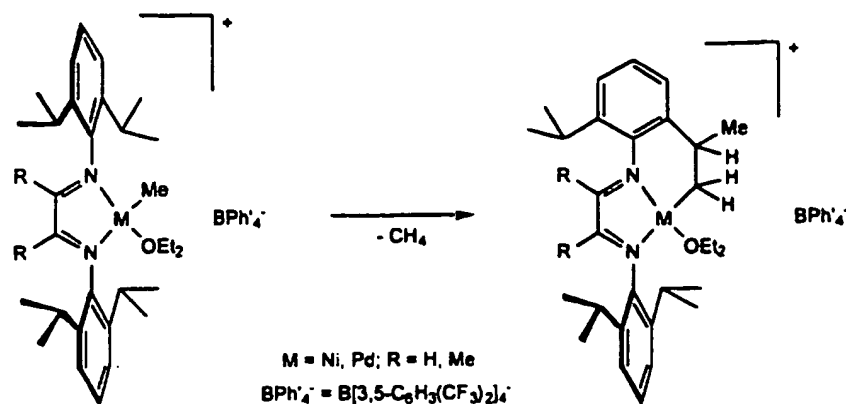
equiv of methyl acrylate were added to the cold tube in subsequent additions via gastight microliter syringe. The tube was transferred to the cold NMR probe. Insertion of methyl acrylate and formation of the 4-membered chelate complex,  $\{[(2,6\text{-i-PrPh})_2\text{DABH}_2]\text{Ni}[\text{CH}(\text{EtC}(\text{O})\text{OMe})]\text{BAF}\}$ , was complete at  $-10^\circ\text{C}$ :  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 400 MHz,  $-10^\circ\text{C}$ )  $\delta$  8.23 and 8.03 (s, 1 each,  $\text{N}=\text{C}(\text{H})-\text{C}'(\text{H})=\text{N}$ ), 7.72 (s, 8, BAF:  $\text{H}_\text{O}$ ), 7.55 (s, 4, BAF:  $\text{H}_\text{P}$ ), 7.5 - 7.2 (m, 6,  $\text{H}_{\text{aryl}}$ ), 3.69, 3.51, 3.34 and 3.04 (septet, 1 each,  $\text{CHMe}_2$ ,  $\text{C}'\text{HMe}_2$ ,  $\text{C}''\text{HMe}_2$  and  $\text{C}''' \text{HMe}_2$ ), 3.58 (s, 3, OMe), 1.48, 1.46, 1.46, 1.45, 1.30, 1.27, 1.193 and 1.189 (d, 3 each,  $\text{J} = 6.5 - 7.3$ ,  $\text{CHMeMe}'$ ,  $\text{C}'\text{HMeMe}'$ ,  $\text{C}''\text{HMeMe}'$  and  $\text{C}''' \text{HMeMe}'$ ), 0.79 and -0.52 (m, 1 each,  $\text{CH}(\text{CHH}'\text{CH}_3)$ ), 0.68 (t, 3,  $\text{J} = 6.9$ ,  $\text{CH}(\text{CH}_2\text{CH}_3)$ , (CHet signal was not assigned due to overlap with other protons).

#### Example 402

A solution of the 4-membered chelate complex  $\{[(2,6\text{-i-PrPh})_2\text{DABH}_2]\text{Ni}[\text{CH}(\text{EtC}(\text{O})\text{OMe})]\text{BAF}\}$  was allowed to stand at RT for 1 day. During this time, conversion to the 6-membered chelate complex,  $\{[(2,6\text{-i-PrPh})_2\text{DABH}_2]\text{Ni}[\text{CH}_2\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OMe}]\text{BAF}\}$ , was complete:  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 400 MHz, rt)  $\delta$  8.47 and 8.01 (s, 1 each,  $\text{N}=\text{C}(\text{H})-\text{C}'(\text{H})=\text{N}$ ), 7.72 (s, 8, BAF:  $\text{H}_\text{O}$ ), 7.56 (s, 4, BAF:  $\text{H}_\text{P}$ ), 7.5 - 7.0 (m, 6,  $\text{H}_{\text{aryl}}$ ), 3.61 (s, 3, OMe), 3.45 and 3.09 (septet, 2 each,  $\text{CHMe}_2$  and  $\text{C}'\text{HMe}_2$ ), 2.25 (t, 2,  $\text{J} = 7.3$ ,  $\text{CH}_2\text{C}(\text{O})$ ), 1.61 (pentet, 2,  $\text{J} = 7.3$ ,  $\text{NiCH}_2\text{CH}_2\text{CH}_2$ ), 1.50, 1.50, 1.46, and 1.30 (d, 6 each,  $\text{J} = 6.8 - 6.9$ ,  $\text{CHMeMe}'$ ,  $\text{C}'\text{HMeMe}'$ ), 0.92 (t, 2,  $\text{J} = 7.4$ ,  $\text{NiCH}_2$ ).

#### Examples 403-407

These Examples illustrate the formation of metallacycles of the formula shown on the right side of the equation, and the use of these metallacycles as polymerization catalysts.



(R = H, Me, An; M = Ni, Pd)

In the absence of olefin, the ether-stabilized catalyst derivatives were observed to decompose in  $\text{CD}_2\text{Cl}_2$  solution with loss of methane. For the catalyst derivative where M = Pd and R = H, methane loss was accompanied by clean and selective formation of the metallacycle resulting from C-H activation of one of the aryl *i*-propyl substituents. This metallacycle could be isolated, although not cleanly, as its instability and high solubility prevented recrystallization. Also it could be converted to another metallacycle in which the diethyl ether ligand is replaced by an olefin ligand, especially ethylene.

#### Example 403

A 700  $\mu\text{L}$   $\text{CD}_2\text{Cl}_2$  solution of  $\{[(2,6\text{-}i\text{-PrPh})_2\text{DABH}_2]\text{PdMe}(\text{OEt}_2)\}\text{BAF}$  (68.4 mg) was allowed to stand at room temperature for several hours and then at  $-30^\circ\text{C}$  overnight. Such highly concentrated solutions of the resulting metallacycle wherein R is H and M is Pd were stable for hours at room temperature, enabling  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra to be acquired:  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 400 MHz,  $41^\circ\text{C}$ )  $\delta$  8.17 (s, 2,  $\text{N}=\text{C}(\text{H})-\text{C}'(\text{H})=\text{N}$ ), 7.75 (s, 8, BAF:  $\text{H}_\text{O}$ ), 7.58 (s, 4, BAF:  $\text{H}_\text{P}$ ), 7.5 - 7.0 (m, 6,  $\text{H}_{\text{aryl}}$ ), 3.48 (q, 4,  $J = 6.88$ ,  $\text{O}(\text{CH}_2\text{CH}_3)_2$ ), 3.26 (septet, 1,  $J = 6.49$ ,  $\text{CHMe}_2$ ), 3.08 (septet, 1,  $J = 6.86$ ,  $\text{C}'\text{HMe}_2$ ), 2.94 (septet, 1,  $J = 6.65$ ,  $\text{C}''\text{HMe}_2$ ), 2.70 (dd, 1,  $J = 6.67$ , 0.90,  $\text{CHMeCHH}'\text{Pd}$ ), 2.43 (dd, 1,  $J = 7.12$ , 4.28,  $\text{CHMeCHH}'\text{Pd}$ ), 2.23 (br m, 1,  $\text{CHMeCH}_2\text{Pd}$ ),

1.54 (d, 3,  $J = 6.86$ ,  $\text{CHMeCH}_2\text{Pd}$ ), 1.43 (d, 3,  $J = 6.79$ ,  $\text{C}'\text{HMeMe}'$ ), 1.40 (d, 3,  $J = 7.12$ ,  $\text{CHMeMe}'$ ), 1.37 (d, 3,  $J = 6.95$ ,  $\text{C}'\text{HMeMe}'$ ), 1.27 (d, 6,  $J = 6.79$ ,  $\text{C}'\text{HMeMe}'$ ,  $\text{C}'\text{HMeMe}'$ ), 1.12 (d, 3,  $J = 6.54$ ,  $\text{CHMeMe}'$ ), 1.23 (br m, 5 6,  $\text{O}(\text{CH}_2\text{CH}_3)_2$ ), 0.21 ( $\text{CH}_4$ );  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 400 MHz, 41 °C)  $\delta$  162.5 ( $J_{\text{CH}} = 181.5$ ,  $\text{N}=\text{C}(\text{H})$ ), 162.3 (q,  $J_{\text{BC}} = 49.8$ , BAF: Cipso), 161.2 ( $J_{\text{CH}} = 178.4$ ,  $\text{N}=\text{C}'(\text{H})$ ), 145.8 and 144.5 (Ar, Ar': Cipso), 141.6, 140.7, 140.3 and 138.8 (Ar, Ar': Cipso), 135.3 (BAF:  $\text{C}_\text{O}$ ), 131.6 and 10 129.8 (Ar, Ar':  $\text{C}_\text{p}$ ), 129.4 (q,  $J_{\text{CF}} = 29.9$ , BAF:  $\text{CF}_3$ ), 128.1, 127.6, 125.2 and 124.5 (Ar, Ar':  $\text{C}_\text{O}$ ,  $\text{C}_\text{O}'$ ), 125.1 (BAF:  $\text{CF}_3$ ), 118.0 (BAF:  $\text{C}_\text{p}$ ), 72 (br,  $\text{O}(\text{CH}_2\text{CH}_3)_2$ ), 43.2 ( $\text{CHMeCH}_2\text{Pd}$ ), 40.5 ( $\text{CHMeCH}_2\text{Pd}$ ), 29.5, 29.1 and 28.8 ( $\text{CHMe}_2$ ,  $\text{C}'\text{HMe}_2$ ,  $\text{C}'\text{HMe}_2$ ), 26.2 (br), 25.3, 25.2, 25.1, 15 24.5 (br), 23.3 and 22.1 ( $\text{CHMeMe}'$ ,  $\text{C}'\text{HMeMe}'$ ,  $\text{C}'\text{HMeMe}'$ ,  $\text{CHMeCH}_2\text{Pd}$ ), 15.5 (br,  $\text{O}(\text{CH}_2\text{CH}_3)_2$ ), -14.8 ( $\text{CH}_4$ ).

#### Example 404

Addition of ethylene to a  $\text{CD}_2\text{Cl}_2$  solution of the compound prepared in Example 403 resulted in loss of 20 ether and formation of the corresponding ethylene adduct (spectral data: see Example 405.) Warming of the ethylene adduct in the presence of excess ethylene resulted in branched polymer formation: 1.3 ppm ( $\text{CH}_2$ )<sub>n</sub>, 0.9 ppm ( $\text{CH}_3$ ). For the ethylene polymerization 25 initiated by this metallacycle, rates of initiation were significantly slower than rates of propagation.

#### Example 405

The metallacycle of Example 403 wherein the diethyl ether ligand was replaced by an ethylene ligand 30 was stable enough so that NMR spectra could be obtained.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 400 MHz, -61 °C)  $\delta$  8.25 and 8.23 ( $\text{N}=\text{C}(\text{H})-\text{C}'(\text{H})=\text{N}$ ), 7.74 (s, 8, BAF:  $\text{H}_\text{O}$ ), 7.55 (s, 4, BAF:  $\text{H}_\text{p}$ ), 7.55 - 7.16 (m, 6,  $\text{H}_{\text{aryl}}$ ), 4.67 (m, 2,  $\text{HH}'\text{C}=\text{CHH}'$ ), 4.40 (m, 2,  $\text{HH}'\text{C}=\text{CHH}'$ ), 2.95 (septet, 1,  $J = 6.30$ ,  $\text{CHMe}_2$ ), 2.80 (septet, 2,  $J = 6.36$ ,  $\text{C}'\text{HMe}_2$  and 35  $\text{C}'\text{HMe}_2$ ), 2.53 (br m, 1,  $\text{CHMeCH}_2\text{Pd}$ ), 2.43 (d, 1,  $J = 8.16$ ,  $\text{CHMeCHH}'\text{Pd}$ ), 1.73 (dd, 1,  $J = 8.16$ , 2.84,  $\text{CHMeCHH}'\text{Pd}$ ), 1.45 and 1.19 (d, 3 each,  $J = 6.79 - 6.40$ ,

CHMeMe'), 1.42 (d, 3, J = 7.05, CHMeCH<sub>2</sub>Pd), 1.30, 1.30, 1.19 and 0.99 (d, 3 each, J = 6.40 - 6.65, C'HMeMe' and C''HMeMe'); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz, -61 °C) δ 162.7 (J<sub>CH</sub> = 179.7, N=CH), 162.1 (J<sub>CH</sub> = 180.9, N=C'H), 161.6 (q, J<sub>CB</sub> = 49.7, BAF: Cipso), 144.7, 141.7, 141.2, 139.2, 137.5 and 137.1 (Ar, Ar': Cipso, Co, C'o), 134.6 (BAF: Co), 131.0 and 129.0 (Ar, Ar': Cp), 128.6 (q, BAF: C<sub>m</sub>), 124.4 (q, J<sub>CF</sub> = 272.5, BAF: CF<sub>3</sub>), 124.6 and 124.0 (Ar, Ar': C<sub>m</sub>), 117.4 (BAF: Cp), 92.3 (J<sub>CH</sub> = 162.4, H<sub>2</sub>C=CH<sub>2</sub>), 45.1 (CH<sub>2</sub>Pd), 41.1 (CHMeCH<sub>2</sub>Pd), 28.9, 28.5 and 28.2 (CHMe<sub>2</sub>, C'HMe<sub>2</sub>, C''HMe<sub>2</sub>), 26.1, 25.6, 25.1, 24.9, 24.6, 22.9 and 21.4 (CHMeMe', C'HMeMe', C''HMeMe', CHMeCH<sub>2</sub>Pd).

#### Example 406

In a nitrogen-filled drybox, 30 mL of THF was added to a flask containing (2,6-i-PrPh)<sub>2</sub>DABAn (1.87 g, 3.72 mmol) and Ni(COD)<sub>2</sub> (1.02 g, 3.72 mmol). The resulting purple solution was stirred for several hours before removing the solvent in vacuo. The product was dissolved in a minimum amount of pentane and the resulting solution was filtered and then placed in the drybox freezer (-35°C) to recrystallize. Purple crystals of [(2,6-i-PrPh)<sub>2</sub>DABAn]Ni(COD) were isolated (1.33 g, 53.5%, first crop). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 MHz, rt) δ 7.77 (d, 2, J = 8.06, H<sub>aryl</sub>), 7.44 (t, 2, J = 7.52, H<sub>aryl</sub>), 7.33 (d, 2, J = 7.70, H<sub>aryl</sub>), 6.89 (t, 2, J = 7.70, H<sub>aryl</sub>), 6.13 (d, 2, J = 6.13, H<sub>aryl</sub>), 3.93 (br s, 4, COD: -HC=CH-), 3.48 (septet, 4, J = 6.87, CHMe<sub>2</sub>), 2.54 (br m, 4, COD: -CHH'-), 1.51 (m, 4, COD: -CHH'-), 1.37 (d, 12, J = 6.60, CHMeMe'), 0.77 (d, 12, J = 6.60, CHMeMe'); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 75.5 MHz, rt) δ 151.7, 151.6, 138.5, 137.1, 133.0, 132.1, 128.8, 125.6, 123.8, 123.7, 119.0 (C<sub>aryl</sub>), 88.7 (COD: -HC=CH-), 29.9 (COD: -CH<sub>2</sub>-), 28.0, 25.1 and 23.8 (CHMeMe').

#### Example 407

In the drybox, a glass insert was loaded with 35.2 mg (0.0527 mmol) of [(2,6-i-PrPh)<sub>2</sub>DABAn]Ni(COD) and 55.2 mg (0.0545 mmol) of H(OEt<sub>2</sub>)<sub>2</sub>BAF. The insert was

cooled to  $-35^{\circ}\text{C}$  in the drybox freezer, 5 mL of  $\text{CDCl}_3$  was added to the cold insert, and the insert was then capped and sealed. Outside of the drybox, the cold tube was placed under 6.9 MPa of ethylene and allowed to warm to rt as it was shaken mechanically for 18 h. An aliquot of the solution was used to acquire a  $^1\text{H}$  NMR spectrum. The remaining portion was added to  $\sim 20$  mL of MeOH in order to precipitate the polymer. The polyethylene (6.1 g) was isolated and dried under vacuum.

#### Examples 408-412

(acac)NiEt(PPh<sub>3</sub>) was synthesized according to published procedures (Cotton, F. A.; Frenz, B. A.; Hunter, D. L. J. Am. Chem. Soc. 1974, 96, 4820-4825).

General Polymerization Procedure for Examples 408-412. In the drybox, a glass insert was loaded with 26.9 mg (0.06 mmol) of (acac)NiEt(PPh<sub>3</sub>), 53.2 mg (0.06 mmol) of NaBAF, and 0.06 mmol of an  $\alpha$ -diimine ligand. In addition, 2 equiv of a phosphine scavenger such as BPh<sub>3</sub> or CuCl was sometimes added. The insert was cooled to  $-35^{\circ}\text{C}$  in the drybox freezer, 5 mL of  $\text{C}_6\text{D}_6$  was added to the cold insert, and the insert was then capped and sealed. Outside of the drybox, the cold tube was placed under 6.9 MPa of ethylene and allowed to warm to RT as it was shaken mechanically for 18 h. An aliquot of the solution was used to acquire a  $^1\text{H}$  NMR spectrum. The remaining portion was added to  $\sim 20$  mL of MeOH in order to precipitate the polymer. The polyethylene was isolated and dried under vacuum.

#### Example 408

The  $\alpha$ -diimine was (2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>. Solid white polyethylene (1.6 g) was isolated.

#### Example 409

The  $\alpha$ -diimine was (2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>, and 29.1 mg of BPh<sub>3</sub> was also added. Solid white polyethylene (7.5 g) was isolated.

Example 410

The  $\alpha$ -diimine was (2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>, and 11.9 of CuCl was also added. Solid white polyethylene (0.8 g) was isolated.

5

Example 411

The  $\alpha$ -diimine was (2,6-i-PrPh)<sub>2</sub>DABAn. Solid white polyethylene (0.2 g) was isolated.

Example 412

10 The  $\alpha$ -diimine was (2,6-i-PrPh)<sub>2</sub>DABAn, and 29.1 mg of BPh<sub>3</sub> was also added. Solid white polyethylene (14.7 g) was isolated.

Examples 413-420

The following synthetic methods and polymerization procedures were used to synthesize and test the  
15 polymerization activity of the functionalized  $\alpha$ -diimine ligands of these Examples.

Synthetic Method A. One equiv of glyoxal or the diketone was dissolved in methanol. Two equiv of the functionalized aniline was added to the solution along  
20 with ~1 mL of formic acid. The solution was stirred until a precipitate formed. The precipitate was collected on a frit and washed with methanol. The product was then dissolved in dichloromethane and the resulting solution was stirred overnight over sodium  
25 sulfate. The solution was filtered and the solvent was removed in vacuo to yield the functionalized  $\alpha$ -diimine.

Synthetic Method B. One equiv of glyoxal or the diketone was dissolved in dichloromethane and two equiv of the functionalized aniline was added to the  
30 solution. The reaction mixture was stirred over sodium sulfate (~1 week). The solution was filtered and the solvent was removed in vacuo. The product was washed or recrystallized from petroleum ether and then dried in vacuo.

Nickel Polymerization Procedure. In the drybox, a glass insert was loaded with one equiv each of  $\text{Ni}(\text{COD})_2$ ,  $\text{H}(\text{OEt}_2)_2\text{BAF}$ , and the  $\alpha$ -diimine ligand. The insert was cooled to  $-35^\circ\text{C}$  in the drybox freezer, 5 mL of  $\text{C}_6\text{D}_6$  was added to the cold insert, and the insert was then capped and sealed. Outside of the drybox, the cold tube was placed under 6.9 MPa of ethylene and allowed to warm to RT as it was shaken mechanically for 18 h. An aliquot of the solution was used to acquire a  $^1\text{H}$  NMR spectrum. The remaining portion was added to ~20 mL of MeOH in order to precipitate the polymer. The polyethylene was isolated and dried under vacuum.

Palladium Polymerization Procedure. In the drybox, a glass insert was loaded with one equiv each of  $[\text{CODPdMe}(\text{NCMe})]\text{BAF}$  and the  $\alpha$ -diimine ligand. The insert was cooled to  $-35^\circ\text{C}$  in the drybox freezer, 5 mL of  $\text{C}_6\text{D}_6$  was added to the cold insert, and the insert was then capped and sealed. Outside of the drybox, the cold tube was placed under 6.9 MPa of ethylene and allowed to warm to RT as it was shaken mechanically for 18 h. An aliquot of the solution was used to acquire a  $^1\text{H}$  NMR spectrum. The remaining portion was added to ~20 mL of MeOH in order to precipitate the polymer. The polyethylene was isolated and dried under vacuum.

25 Example 413

$\alpha$ -Diimine was  $(2\text{-hydroxyethylPh})_2\text{DABMe}_2$ .  
Synthetic Method B:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz, rt)  $\delta$  7.28 - 7.20 (m, 4,  $\text{H}_{\text{aryl}}$ ), 7.12 (t, 2,  $J = 7.52$ ,  $\text{H}_{\text{aryl}}$ ), 6.67 (d, 2,  $J = 7.67$ ,  $\text{H}_{\text{aryl}}$ ), 3.74 (t, 4,  $J = 6.79$ ,  $\text{CH}_2\text{OH}$ ), 3.11 (br s, 2, OH), 2.76 (t, 4,  $J = 6.79$ ,  $\text{CH}_2\text{CH}_2\text{OH}$ ), 2.16 (s, 6,  $\text{N}=\text{C}(\text{Me})-\text{C}(\text{Me})=\text{N}$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz, rt)  $\delta$  168.2 ( $\text{N}=\text{C}-\text{C}=\text{N}$ ), 149.0 (Ar: C<sub>ipso</sub>), 128.4 (Ar: C<sub>O</sub>), 130.4, 127.1, 124.6 and 118.2 (Ar: C<sub>m</sub>, C<sub>p</sub>, C<sub>m'</sub>, C<sub>O'</sub>), 62.9 ( $\text{CH}_2\text{OH}$ ), 35.3 ( $\text{CH}_2\text{CH}_2\text{OH}$ ), 15.8 ( $\text{N}=\text{C}(\text{Me})-\text{C}(\text{Me})=\text{N}$ ).

Nickel Polymerization Procedure: (0.02 mmol scale) Seventy mg of polyethylene was isolated.  $^1\text{H}$

NMR spectrum ( $C_6D_6$ ) shows the production of 1- and 2-butenes along with smaller amounts of higher olefins.

Palladium Polymerization Procedure: (0.06 mmol scale) No polymer was isolated, however, the  $^1H$  NMR spectrum shows peaks consistent with the formation of branched polyethylene: 1.3 ppm ( $(CH_2)_n$ ), 0.9 ppm ( $CH_3$  of branches). Broad  $\alpha$ -olefinic resonances are observed in the baseline.

#### Example 414

10  $\alpha$ -Diimine is (2,6-Et-3,5-chloroPh) $_2$ DABMe $_2$ .  
 Synthetic Method A:  $^1H$  NMR ( $CDCl_3$ , 300 MHz, rt)  $\delta$  7.19 (s, 1, H $_{aryl}$ ), 2.64 (sextet, 4, J = 7.19, CHH'CH $_3$ ), 2.36 (sextet, 4, J = 7.11, CHH'CH $_3$ ), 2.10 (s, 6, N=C(Me)-C(Me)=N), 1.05 (t, 12, J = 7.52, CH $_2$ CH $_3$ );  $^{13}C$   
 15 NMR ( $CDCl_3$ , 75 MHz, rt)  $\delta$  168.8 (N=C-C=N), 149.3 (Ar: Cipso), 132.3 and 127.4 (Ar: C $_O$  and C $_m$ ), 124.7 (Ar: C $_p$ ), 22.5 (CH $_2$ CH $_3$ ), 16.8 (N=C(Me)-C(Me)=N), 12.1 (CH $_2$ CH $_3$ ).

Nickel Polymerization Procedure: (0.06 mmol scale) Solid white polyethylene (14.6 g) was isolated.

Palladium Polymerization Procedure: (0.06 mmol scale) Polyethylene (0.06 g) was isolated as an oil.  $^1H$  NMR spectrum ( $C_6D_6$ ) shows branched polyethylene along with some internal olefinic end groups.

25 Palladium Polymerization Procedure: {0.03 mmol scale; Isolated [(2,6-Et-3,5-chloroPh) $_2$ DABMe $_2$ ][PdMe(NCMe)]BAF was used.} Polyethylene (2.42 g) was isolated as an oil.

#### Example 415

30  $\alpha$ -Diimine is (2,6-Et-3-chloroPh) $_2$ DABMe $_2$ . Synthetic Method A:  $^1H$  NMR ( $CDCl_3$ , 300 MHz, rt)  $\delta$  7.10 (d, 2, J = 8.43, H $_{aryl}$ ), 7.04 (d, 2, J = 8.07, H $_{aryl}$ ), 2.65 (m, 2, CHH'CH $_3$ ), 2.49 (m, 2, CHH'CH $_3$ ), 2.30 (m, 4, C'HH'C'H $_3$ ), 2.08 (s, 6, N=C(Me)-C(Me)=N), 1.15 and 1.07 (t, 6 each, J = 7.52, CH $_2$ CH $_3$  and C'H $_2$ C'H $_3$ );  $^{13}C$  NMR ( $CDCl_3$ , 75 MHz, rt)  $\delta$  168.4 (N=C-C=N), 148.5 (Ar: Cipso), 132.0, 129.1 and 128.6 (Ar: C $_O$ , C $_O'$ , C $_m$ ), 126.9



and 124.3 (Ar: C<sub>m</sub>' and C<sub>p</sub>), 24.4 and 22.6 (CH<sub>2</sub>CH<sub>3</sub> and C'H<sub>2</sub>C'H<sub>3</sub>), 16.5 (N=C(Me)-C(Me)=N), 13.4 and 12.4 (CH<sub>2</sub>CH<sub>3</sub> and C'H<sub>2</sub>C'H<sub>3</sub>).

Palladium Polymerization Procedure: {0.03 mmol

- 5 scale; Isolated [(2,6-Et-3-chloroPh)<sub>2</sub>DABMe<sub>2</sub>)PdMe(NCMe)]BAF was used.}  
Polyethylene (~1 g) was isolated as an amorphous solid.

Example 416

- α-Diimine is (2,6-bromo-4-MePh)<sub>2</sub>DABMe<sub>2</sub>. Synthetic  
10 Method A: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, rt) δ 7.40 (m, 4, Haryl), 2.32 (s, 6, Ar: Me), 2.14 (s, 6, N=C(Me)-C(Me)=N); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, rt) δ 171.5 (N=C-C=N), 144.9 (Ar: Cipso), 135.7 (Ar: C<sub>p</sub>), 132.4 (Ar: C<sub>m</sub>), 112.3 (Ar: C<sub>o</sub>), 20.2 and 16.9 (N=C(Me)-C(Me)=N and  
15 Ar: Me)

Nickel Polymerization Procedure: (0.02 mmol

- scale) Solid white polyethylene (5.9 g) was isolated.  
<sup>1</sup>H NMR spectrum (C<sub>6</sub>D<sub>6</sub>) shows a significant amount of  
20 branched polymer along with internal olefinic end groups.

Palladium Polymerization Procedure: (0.06 mmol

- scale) Polyethylene (0.38 g) was isolated as an oil.  
<sup>1</sup>H NMR spectrum (C<sub>6</sub>D<sub>6</sub>) shows a significant amount of  
25 branched polymer along with internal olefinic end groups.

Example 417

- α-Diimine is (2,6-Me-4-bromoPh)<sub>2</sub>DABH<sub>2</sub>. Synthetic  
Method A: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, rt) δ 8.07 (s, 2, N=CH-CH=N), 7.24 (s, 4, Haryl), 2.15 (s, 12, Ar: Me);  
30 <sup>13</sup>C NMR (CDCl<sub>3</sub>, 300 MHz, rt) δ 163.6 (N=C-C=N), 148.7 (Ar: Cipso), 131.0 and 128.7 (Ar: C<sub>o</sub> and C<sub>m</sub>), 117.7 (Ar: C<sub>p</sub>), 18.1 (Ar: Me).

Nickel Polymerization Procedure: (0.06 mmol

- scale) Solid white polyethylene (9.5 g) was isolated.

- 35 Palladium Polymerization Procedure: (0.06 mmol scale) No polymer was isolated, however, the <sup>1</sup>H NMR spectrum (C<sub>6</sub>D<sub>6</sub>) shows the production of α- and internal olefins (butenes and higher olefins). A small

resonance exists at 1.3 ppm and is consistent with the resonance for  $(CH_2)_n$ .

Example 418

$\alpha$ -Diimine is (2,6-Me-4-bromoPh)<sub>2</sub>DABMe<sub>2</sub>. Synthetic  
5 Method A: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, rt)  $\delta$  7.22 (s, 4, Haryl), 2.02 (s, 6, N=C(Me)-C(Me)=N), 2.00 (s, 12, Ar: Me); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, rt)  $\delta$  168.5 (N=C-C=N), 147.3 (Ar: Cipso), 130.6 (Ar: C<sub>m</sub>), 126.9 (Ar: C<sub>o</sub>), 115.9 (Ar: C<sub>p</sub>), 17.6 (Ar: Me), 15.9 (N=C(Me)-C(Me)=N).

10 Nickel Polymerization Procedure: (0.06 mmol scale) Solid white polyethylene (14.9 g) was isolated.

Palladium Polymerization Procedure: (0.06 mmol scale) Polyethylene (1.3 g) was isolated as an oil. The <sup>1</sup>H NMR spectrum (C<sub>6</sub>D<sub>6</sub>) shows resonances consistent  
15 with the formation of branched polymer. Resonances consistent with olefinic end groups are observed in the baseline.

Palladium Polymerization Procedure: {0.03 mmol scale; Isolated[(2,6-Me-4-bromoPh)<sub>2</sub>DABMe<sub>2</sub>)PdMe(NCMe)]BAF was used.}  
20 Polyethylene (3.97 g) was isolated as a mixture of a soft white solid and an amorphous oil. <sup>1</sup>H NMR spectrum (C<sub>6</sub>D<sub>6</sub>) shows branched polyethylene.

Example 419

25

$\alpha$ -Diimine is (2-Me-6-chloroPh)<sub>2</sub>DABMe<sub>2</sub>.

Nickel Polymerization Procedure: (0.02 mmol scale) Solid white polyethylene (220 mg) was isolated. In addition, the <sup>1</sup>H NMR spectrum (C<sub>6</sub>D<sub>6</sub>) shows the  
30 production of 1- and 2-butenes.

Palladium Polymerization Procedure: (0.03 mmol scale; Isolated [(2-Me-6-chloroPh)<sub>2</sub>DABMe<sub>2</sub>]PdMe(NCMe)]SbF<sub>6</sub> was used.)

Polyethylene (3.39 g) was isolated as an oil. The <sup>1</sup>H NMR spectrum (C<sub>6</sub>D<sub>6</sub>) shows the production of branched polyethylene; internal olefin end groups are also present.

Example 420

(2,6-t-BuPh)<sub>2</sub>DABAN

10 This compound was made by a procedure similar to that of Example 25. Two g (9.74 mmol) of 2,5-di-t-butylaniline and 0.88 g (4.8 mmol) of acenaphthenequinone were partially dissolved in 50 mL of methanol. Attempted crystallization from ether and  
15 from CH<sub>2</sub>Cl<sub>2</sub> yielded an orange/yellow powder (1.75 g, 66%--not optimized). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz) δ 7.85 (d, 2H, J = 8.1 Hz, BIAN: H<sub>p</sub>), 7.44 (d, 2H, J = 8.4 Hz, Ar: H<sub>m</sub>), 7.33 (dd, 2H, J = 8.4, 7.3 Hz, BIAN: H<sub>m</sub>), 7.20 (dd, 2H, J = 8.1, 2.2 Hz, Ar: H<sub>p</sub>), 6.99 (d, 2H, J = 2.2  
20 Hz, Ar: H<sub>o</sub>), 6.86 (d, 2H, J = 7.0 Hz, BIAN: H<sub>o</sub>), 1.37, 1.27 (s, 18H each, C(CH<sub>3</sub>)<sub>3</sub>).

Example 421

A 100mg sample of {[(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>]PdCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C(O)OCH<sub>3</sub>}<sup>+</sup>BAF<sup>-</sup> in a Schlenk  
25 flask was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (4ml) and cyclopentene (8ml) added. The flask was flushed well with a 10% ethylene in N<sub>2</sub> mix and the solution stirred with a slow flow of the gas mixture passing through the flask. After 15 hours the product had solidified into a single  
30 mass of yellow/brown polymer. The reaction was quenched with MeOH and the polymer broken into pieces and washed with MeOH. Yield = 2.0g. DSC: T<sub>m</sub> = 165°C (32J/g). Integration of the <sup>1</sup>H-NMR spectrum indicated 83 mole% cyclopentene.

35

Example 422

A 37mg sample of [(2,4,6-MePh)<sub>2</sub>DABAN]NiBr<sub>2</sub> in cyclopentene (5ml) was placed in a Schlenk flask under an atmosphere of ethylene. Modified MAO (1.1ml, 7.2wt%

Al) was added and the reaction allowed to run for 16 hours after which time the product had solidified into a mass of green polymer. The reaction was quenched by addition of MeOH/10%HCl and the polymer was crushed and  
5 washed well with MeOH and finally a 2% Irganox/acetone solution. Yield = 3.6g.

Example 423

A 30mg sample of [(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>]NiBr<sub>2</sub> was slurried in toluene (2ml) and norbornene (2g). PMAO  
10 (1ml, 9.6wt% Al) was added. The solution immediately turned deep blue/black and in less than a minute became extremely viscous. The reaction was quenched after 15 hours by addition of MeOH/10%HCl causing the polymer to precipitate. The solid was filtered, washed well with  
15 MeOH and finally with a 2% Irganox® 1010 in acetone solution. The polymer was cut into pieces and dried. Yield = 0.8g (40%). <sup>1</sup>H-NMR (ODCB, 120°C): 1.0-2.5 ppm complex multiplet confirms that the product is an addition polymer. The absence of olefinic peaks  
20 precludes the existence of ROMP product and indicates that the polymer is not of extremely low molecular weight.

Example 424

A 32mg sample of [(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>]CoCl<sub>2</sub> was  
25 slurried in toluene (2ml) and norbornene (4g). PMAO (1.5ml, 9.6wt% Al) was added. The solution immediately turned deep purple and within a few minutes became extremely viscous and difficult to stir. The reaction was quenched after 4 hours by addition of MeOH/10%HCl  
30 causing the polymer to precipitate. The solid was filtered, washed well with MeOH and finally with a 2% Irganox in acetone solution. The polymer was dried overnight at 110°C under vacuum. Yield = 2.1g (53%). It was possible to further purify the product by  
35 dissolving in cyclohexane and reprecipitating with MeOH. <sup>1</sup>H-NMR (TCE, 120°C): 1.0-2.5 ppm complex multiplet.

Example 425

A 33mg sample of  $((2,4,6\text{-MePh})_2\text{DABAN})\text{CoCl}_2$  was slurried in toluene (2ml) and norbornene (4g). PMAO (2.0ml, 9.6wt% Al) was added. The solution immediately turned deep blue and within a few minutes the viscosity began to increase. The reaction was quenched after 4 hours by addition of MeOH/10%HCl causing the polymer to precipitate. The solid was filtered, washed well with MeOH and finally with a 2% Irganox® 1010 in acetone solution. The polymer was dried overnight at 110°C under vacuum. Yield = 0.8g (13%). It was possible to further purify the product by dissolving in cyclohexane and reprecipitating with MeOH.  $^1\text{H-NMR}$  (TCE, 120°C): 1.0-2.5 ppm complex multiplet.

Example 426

A 23mg sample of  $[(2,4,6\text{-MePh})_2\text{DABH}_2]\text{PdMeCl}$  was slurried in toluene (2ml) and norbornene (2.7g). PMAO (1.0mL, 9.6wt% Al) was added. Solids immediately formed and after a few seconds stirring stopped. The reaction was quenched after 2 hours by addition of MeOH/10%HCl. The solid was filtered, crushed and washed well with MeOH and finally with a 2% Irganox® 1010 in acetone solution. Yield = 2.5g (92%).

Example 427

A 16mg sample of  $[(2,4,6\text{-MePh})_2\text{DABH}_2]\text{NiBr}_2$  was slurried in dicyclopentadiene (~3g). MMAO (1.2ml, 7.2wt% Al) was added. Solution immediately turned deep red/purple and started to foam. The reaction was quenched after 16 hours by addition of MeOH/10%HCl which precipitated the polymer. The solid was filtered and washed well with MeOH and finally with a 2% Irganox® 1010 in acetone solution. Yield = 0.25g.

Example 428

A 20mg sample of  $[(2,4,6\text{-MePh})_2\text{DABH}_2]\text{PdMeCl}$  was slurried in toluene (2ml) and ethylidene norbornene (2 ml). PMAO (1.0mL, 9.6wt% Al) was added. The solution turned a pale orange and after an hour the viscosity had increased. After 14 hours the mixture had

solidified into a gel and stirring had stopped. The reaction was quenched by addition of MeOH/10% HCl. The solid was filtered, crushed and washed well with MeOH and finally with a 2% Irganox® 1010 in acetone solution. Yield = 0.7g (39%).

Example 429

NiI<sub>2</sub> (0.26g) was placed in THF (10ml) and (2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub> (340mg) was added. The resulting mixture was stirred for 2 days after which the THF was removed and pentane added. The red/brown solid was isolated by filtration and washed several times with pentane. Yield = 0.53g (89%).

A portion of the product (9 mg) in toluene (25mL) in a Schlenk flask was placed under an atmosphere of ethylene (140 kPa [absolute]) and 0.25 ml PMAO solution (9.6% Al) was added. The solution turned dark green and, after several hours at room temperature, became viscous. After 16 hours the reaction was quenched with MeOH/10% HCl which precipitated the polymer. The polymer (1.25g) was collected by filtration, washed well with MeOH and dried under reduced pressure. <sup>1</sup>H NMR indicated -133 methyl per 1000 methylene.

Example 430

CoI<sub>2</sub> (286mg) was dissolved in THF (10ml) and (2,6-iPrPh)<sub>2</sub>DABMe<sub>2</sub> (370mg) was added. The resulting mixture was stirred for 3 days after which the THF was removed and pentane added. The brown solid was isolated by filtration and washed several times with pentane. Yield = 0.29g (44%). <sup>1</sup>H NMR (THF-d<sub>8</sub>) 1.0-1.4 (m, 24H, CH-CH<sub>3</sub>), 2.06 (s, 6H, N=C-CH<sub>3</sub>), 2.6-2.8 (m, 4H, C-CH-(CH<sub>3</sub>)<sub>2</sub>), 7.0-7.3 (m, 6H, aromatic). This data is consistent with the formula: [(2,6-iPrPh)<sub>2</sub>DABMe<sub>2</sub>]CoI<sub>2</sub>

A portion of the above product (14mg, 0.02mmol) in toluene (25mL) in a Schlenk flask was placed under an atmosphere of ethylene (140 kPa [absolute]) and 0.4 ml PMAO solution (9.6% Al) was added. The solution turned purple and, after several hours at room temperature, became viscous. After 18 hours the reaction was

quenched with MeOH/10% HCl which precipitated the polymer. The polymer (634mg) was collected by filtration, washed well with MeOH and dried under reduced pressure.  $^1\text{H}$  NMR indicated ~ 100 methyl per 1000 methylene. DSC:  $T_g = -45^\circ\text{C}$ .

Example 431

Solid  $\pi$ -cyclooctenyl-1,5-cyclooctadienecobalt (I) (17mg, 0.06mmol) (prepared according to: Gosser L., Inorg. Synth., 17, 112-15, 1977) and solid (2,6- $i\text{PrPh}$ )<sub>2</sub>DABMe<sub>2</sub> (24mg, 0.06mmol) were placed in a Schlenk flask and toluene (25mL) added. An ethylene atmosphere was admitted (34 kPa gauge) and the solution stirred for 5 minutes. The final color was brown/green. 0.8 ml PMAO solution (9.6% Al) was added. After 18 hours the reaction was quenched with MeOH/10% HCl which precipitated the polymer. The polymer (190mg) was collected by filtration, washed well with MeOH and dried under reduced pressure.  $^1\text{H}$  NMR indicated 90 methyl per 1000 methylene. DSC:  $T_g = -45^\circ\text{C}$ .

Example 432

[(2,6- $i\text{PrPh}$ )<sub>2</sub>DABMe<sub>2</sub>]<sub>2</sub>CoCl<sub>2</sub> (619mg) was slurried in Et<sub>2</sub>O (5ml) and cooled to  $-25^\circ\text{C}$ . Me<sub>2</sub>Mg (63mg in 5ml Et<sub>2</sub>O) was added and the solution stirred for 15 minutes. Et<sub>2</sub>O was removed under reduced pressure and the resulting bright purple solid was dissolved in pentane, filtered to remove MgCl<sub>2</sub> and the volume reduced to 5 ml. The solution was cooled to  $-25^\circ\text{C}$  for 2 days and the resulting purple crystals isolated by filtration. Yield = 420mg (73%). Crystal structure determination confirmed that the product was [(2,6- $i\text{PrPh}$ )<sub>2</sub>DABMe<sub>2</sub>]<sub>2</sub>CoMe<sub>2</sub>.

[(2,6- $i\text{PrPh}$ )<sub>2</sub>DABMe<sub>2</sub>]<sub>2</sub>CoMe<sub>2</sub> (34mg) in toluene (25mL) in a Schlenk flask was placed under an atmosphere of ethylene (140 kPa [absolute]) and after stirring for 2 hours, 0.6 ml PMAO solution (9.6% Al) was added. The solution remained dark purple and, after several hours at room temperature, became viscous. After 48 hours the reaction was quenched with MeOH/10% HCl which

precipitated the polymer. The polymer (0.838g) was collected by filtration, washed well with MeOH and dried under reduced pressure. Branching ( $^1\text{H-NMR}$ ): 115 methyl per 1000 methylene. DSC:  $T_g = -45^\circ\text{C}$ .

5

Example 433

[(2,6-*i*PrPh) $_2$ DABMe $_2$ ]CoMe $_2$  (30mg) was dissolved in benzene (10ml in a shaker tube) and the solution frozen. Montmorillonite K-10 (Aldrich Chemical Co., Milwaukee, WI, U.S.A.) (200mg, conditioned at  $140^\circ\text{C}$  for 48hrs under vacuum) suspended in benzene (10ml) was added on top of the frozen layer and frozen as well. The solution was thawed under an ethylene atmosphere (6.9 MPa) and shaken at that pressure for 18 hours. MeOH was added to the resulting polymer which was then isolated by filtration, washed well with MeOH and dried under reduced pressure. Yield = 7.5g crystalline polyethylene. Branching ( $^1\text{H-NMR}$ ): 18 Methyl per 1000 methylene.

10

15

Example 434

[(2,6-*i*PrPh) $_2$ DABMe $_2$ ]CoMe $_2$  (15mg) was dissolved in benzene (10ml in a shaker tube) and the solution frozen. Montmorillonite K-10 (100mg, conditioned at  $600^\circ\text{C}$  for 48hrs under vacuum) suspended in benzene (10ml) was added on top of the frozen layer and frozen as well. The solution was thawed under an ethylene atmosphere (6.9 MPa) and shaken at that pressure for 18 hours. MeOH was added to the resulting polymer which was then isolated by filtration, washed well with MeOH and dried under reduced pressure. Yield = 3g polyethylene. Branching ( $^1\text{H NMR}$ ): 11 Methyl per 1000 methylene.

20

25

30

Example 435

[(2,6-*i*PrPh) $_2$ DABMe $_2$ ]CoMe $_2$  (15mg) was dissolved in benzene (10ml in a shaker tube) and the solution frozen. Tris(pentafluorophenyl)boron (25mg) dissolved in benzene (10ml) was added on top of the frozen layer and frozen as well. The solution was thawed under an ethylene atmosphere (6.9 MPa) and shaken at that

35



pressure for 18 hours. MeOH was added to the resulting polymer which was then isolated by filtration, washed well with MeOH and dried under reduced pressure. Yield = 105mg polyethylene. Branching ( $^1\text{H}$  NMR): 60 Methyl per 1000 methylene.

Example 436

[(2,6-*i*PrPh) $_2$ DABMe $_2$ ]CoMe $_2$  (15mg) was dissolved in benzene (10ml in a shaker tube) and the solution frozen. HBAF $\cdot$ 2Et $_2$ O (30mg) slurried in benzene (10ml) was added on top of the frozen layer and frozen as well. The solution was thawed under an ethylene atmosphere (6.9 MPa) and shaken at that pressure for 18 hours. MeOH was added to the resulting polymer which was then isolated by filtration, washed well with MeOH and dried under reduced pressure. Yield = 3.8g polyethylene. Branching ( $^1\text{H}$  NMR): 21 Methyl per 1000 methylene.

Example 437

CoCl $_2$  (102mg) was placed in acetonitrile and AgBF $_4$  (306mg) added. The solution was stirred for 30 minutes after which the white AgCl was filtered off. (2,6-*i*-PrPh) $_2$ DABMe $_2$  (318mg) was added and the solution stirred overnight. The acetonitrile was removed under reduced pressure and pentane added. The orange product was isolated by filtration and washed and dried.  $^1\text{H}$ -NMR (THF- $d_8$ ): 1.1-1.4 (m, C-CH-CH $_3$ , 24H), 1.8 (CH $_3$ CN, 6H), 2.2 (N=C-CH $_3$ , 6H), 2.7 (m, C-CH-CH $_3$ , 4H), 7.0-7.2 (m, C=CH, 6H). The spectrum is consistent with the molecular formula: [(2,6-*i*PrPh) $_2$ DABMe $_2$ )Co(CH $_3$ CN) $_2$ ](BF $_4$ ) $_2$

A portion of the product (43mg) in toluene (25mL) in a Schlenk flask was placed under an atmosphere of ethylene (35 kPa gauge) and 0.8 ml PMAO solution (9.6% Al) was added. The solution turned dark purple. After 18 hours the reaction was quenched with MeOH/10% HCl which precipitated the polymer. The polymer (0.310g) was collected by filtration, washed well with MeOH and

dried under reduced pressure. Branching ( $^1\text{H}$  NMR): 72 Methyl per 1000 methylene.

Example 438

Solid  $\text{Co(II)}[(\text{CH}_3)_2\text{CHC(O)O}^-]_2$  (17mg, 0.073mmol)  
5 and solid  $(2,6\text{-iPrPh})_2\text{DABMe}_2$  (32mg, 0.079mmol) were placed in a Schlenk flask and toluene (25mL) added. An ethylene atmosphere was admitted (140 kPa [absolute]) and 3.0 ml PMAO solution (9.6% Al) was added. After 18 hours the reaction was quenched with MeOH/10% HCl which  
10 precipitated the polymer. The polymer (57mg) was collected by filtration, washed well with MeOH and dried under reduced pressure.  $^1\text{H}$  NMR indicated 32 methyl per 1000 methylene.

Example 439

15 The complex  $\{[(2,6\text{-EtPh})_2\text{DABMe}_2]\text{PdMe}(\text{NCMe})\}^+\text{SbF}_6^-$  was weighed (50 mg, 0.067 mmol) into a 100 mL round-bottom flask inside a dry box. Cyclopentene (20 mL, 3400 equivalents per Pd; unpurified) and dichloromethane (20 mL) were added to the flask, and  
20 stirred under a nitrogen atmosphere to give a homogeneous solution. A precipitate had formed after 2 days. After 7 days, the solvent was evaporated and the solids were dried in a vacuum oven to give 0.39 g polymer (86 turnovers/Pd). A sample of the polymer was  
25 washed several times with petroleum ether and ether, then dried in a vacuum oven. The polymer was pressed at  $290^\circ\text{C}$  into a transparent, gray-brown, tough film. DSC (0 to  $300^\circ\text{C}$ ,  $10^\circ\text{C}/\text{min}$ , first heat):  $T_g = 120^\circ\text{C}$ ,  $T_m$  (onset to end) =  $179$  to  $232^\circ\text{C}$ , heat of fusion =  $18\text{ J/g}$ .  
30  $^1\text{H}$  NMR (400 MHz,  $120^\circ\text{C}$ , ortho-dichlorobenzene- $d_4$ , referenced to solvent peak at 7.280 ppm): 0.905 (bs, 1H, cis -CH-CH<sub>2</sub>-CH-), 1.321 (bs, 2H, cis -CH-CH<sub>2</sub>-CH<sub>2</sub>-CH-), 1.724 and 1.764 (overlapping bs, 4H, trans -CH-CH<sub>2</sub>-CH<sub>2</sub>-CH- and -CH-CH<sub>2</sub>-CH<sub>2</sub>-CH-), 1.941 (bs, 1H, trans -CH-CH<sub>2</sub>-CH-).  
35 The  $^1\text{H}$  NMR assignments are based upon 2D NMR correlation of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts, and are consistent with a poly(cis-1,3-cyclopentylene) repeat unit.

Example 440

The complex  $\{[(2,6\text{-iPrPh})_2\text{DABAN}]\text{PdMe}(\text{OEt}_2)\}^+\text{SbF}_6^-$  was weighed (50 mg, 0.054 mmol) into a 100 mL round-bottom flask inside a dry box. Cyclopentene (20 mL, 4200 equivalents per Pd; unpurified) and dichloromethane (20 mL) were added to the flask, and stirred under a nitrogen atmosphere to give a homogeneous solution. A precipitate had formed after 3 days. After 6 days, the solvents were evaporated and the solids were dried in a vacuum oven to give 0.20 g polymer (55 turnovers/Pd). A sample of the polymer was washed several times with petroleum ether and ether, then dried in a vacuum oven. DSC (0 to 300°C, 10° C/min, first heat):  $T_g = 42^\circ\text{C}$ ,  $T_m$  (onset to end) = 183 to 242°C, heat of fusion = 18 J/g.  $^1\text{H}$  NMR (400 MHz, 70 °C,  $\text{CDCl}_3$ , referenced to solvent peak at 7.240 ppm): 0.75 (bm, 1H, cis -CH-CH<sub>2</sub>-CH-), 1.20 (bs, 2H, cis -CH-CH<sub>2</sub>-CH<sub>2</sub>-CH-), 1.59 and 1.68 (overlapping bs, 4H, trans -CH-CH<sub>2</sub>-CH<sub>2</sub>-CH- and -CH-CH<sub>2</sub>-CH<sub>2</sub>-CH-), 1.83 (bs, 1H, trans -CH-CH<sub>2</sub>-CH-). The  $^1\text{H}$  NMR assignments are based upon 2D NMR correlation of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts, and are consistent with a poly(cis-1,3-cyclopentylene) repeat unit.

Example 441

The complex  $[(2,6\text{-iPrPh})_2\text{DABMe}_2]\text{PdMeCl}$  was added (28 mg, 0.050 mmol) to a glass vial containing cyclopentene (3.40 g, 1000 equivalents per Pd; distilled twice from Na) inside a dry box. A solution of MMAO in heptane (1.47 mL, 1.7 M Al, 50 equivalents per Pd) was added with stirring to give a homogeneous solution. A precipitate began to form immediately. After 2 days, the solids were collected by vacuum filtration, washed several times on the filter with petroleum ether and ether, then dried in a vacuum oven to give 0.254 g polymer (75 turnovers/Pd). The polymer was pressed at 250°C into a transparent, gray-brown, tough film. DSC (0 to 300°C, 10°C/min, first heat):  $T_g = 114^\circ\text{C}$ ,  $T_m$  (onset to end) = 193 to 240°C, heat of

fusion = 14 J/g. GPC (Dissolved in 1,2,4-trichlorobenzene at 150°C, run in tetrachloroethylene at 100°C, polystyrene calibration): peak MW = 154,000,  $M_n = 70,200$ ,  $M_w = 171,000$ ,  $M_w/M_n = 2.43$ .

5

Example 442

The complex  $\{[(2,6\text{-iPrPh})_2\text{DABMe}_2]\text{PdCH}_2\text{CH}_2\text{CH}_2\text{C(O)OCH}_3\}^+ \text{SbF}_6^-$  was weighed (42 mg, 0.050 mmol) into a glass vial inside a dry box. Cyclopentene (3.40 g, 1000 equivalents per Pd; 10 distilled twice from Na) and dichloromethane (4.4 mL) were added with stirring to give a homogeneous solution. After 1 day, the solids were collected by vacuum filtration, washed several times on the filter with petroleum ether and ether, then dried in a vacuum 15 oven to give 1.605 g polymer (471 turnovers/Pd). The polymer was pressed at 250°C into a transparent, gray-brown, tough film. TGA (25 to 600°C, 10°C/min, nitrogen):  $T_d$  (onset to end) = 473 to 499, 97.06 % weight loss. TGA (25 to 600 °C, 10 °C/min, air):  $T_d =$  20 350°C, 5 % weight loss. DSC (0 to 300 °C, 10°C/min, second heat):  $T_g = 94^\circ\text{C}$ ,  $T_m$  (onset to end) = 191 to 242 °C, heat of fusion = 14 J/g. GPC (Dissolved in 1,2,4-trichlorobenzene at 150°C, run in tetrachloroethylene at 100 °C, polystyrene calibration): peak MW = 152,000, 25  $M_n = 76,000$ ,  $M_w = 136,000$ ,  $M_w/M_n = 1.79$ .

Example 443

The complex  $[(2,6\text{-iPrPh})_2\text{DABMe}_2]\text{PdCl}_2$  was weighed (29 mg, 0.050 mmol) into a glass vial inside a dry box. Cyclopentene was added (6.81 g, 2000 equivalents per 30 Pd; distilled from polyphosphoric acid), and the vial was cooled to <0°C. A solution of MMAO in heptane (1.00 mL, 1.7 M Al, 34 equivalents per Pd) was added with stirring to give a homogeneous solution. After 1 day, a copious precipitate had formed. After 2 days, 35 the solids were collected by vacuum filtration, washed several times on the filter with ether and cyclohexane, then dried in a vacuum oven to give 1.774 g polymer (520 turnovers/Pd). The polymer was coated with 5000

ppm Irganox® 1010 by evaporating an acetone slurry and drying in a vacuum oven. The polymer was pressed at 290°C into a transparent, gray-brown, tough film. DSC (25 to 330°C, 10°C/min, second heat):  $T_g = 105^\circ\text{C}$ ,  $T_m$  (onset to end) = 163 to 244°C, heat of fusion = 21 J/g.

#### Example 444

The complex  $[(2,6\text{-iPrPh})_2\text{DABMe}_2]\text{PdCl}_2$  was weighed (29 mg, 0.050 mmol) into a glass vial inside a dry box. Cyclopentene was added (6.81 g, 2000 equivalents per Pd; distilled from polyphosphoric acid), and the vial was cooled to  $<0^\circ\text{C}$ . A solution of  $\text{EtAlCl}_2$  in hexane (1.7 mL, 1.0 M, 34 equivalents per Pd) was added with stirring to give a homogeneous solution. After 4 days, the solids were collected by vacuum filtration, washed several times on the filter with ether and cyclohexane, then dried in a vacuum oven to give 1.427 g polymer (419 turnovers/Pd). The polymer was coated with 5000 ppm Irganox® 1010 by evaporating an acetone slurry and drying in a vacuum oven. The polymer was pressed at 290°C into a transparent, gray-brown, tough film. DSC (25 to 330°C, 10°C/min, second heat):  $T_g = 103^\circ\text{C}$ ,  $T_m$  (onset to end) = 153 to 256°C, heat of fusion = 23 J/g.

#### Example 445

The complex  $[(2,6\text{-iPrPh})_2\text{DABMe}_2]\text{PdCl}_2$  was weighed (29 mg, 0.050 mmol) into a glass vial inside a dry box. Cyclopentene was added (6.81 g, 2000 equivalents per Pd; distilled from polyphosphoric acid), and the vial was cooled to  $<0^\circ\text{C}$ . A solution of  $\text{EtAlCl}_2$  and  $\text{Et}_2\text{AlCl}$  in toluene (1.9 mL, 0.91 M, 68 equivalents Al per Pd) was added with stirring to give a homogeneous solution. After 4 days, the solids were collected by vacuum filtration, washed several times on the filter with ether and cyclohexane, then dried in a vacuum oven to give 1.460 g polymer (429 turnovers/Pd). The polymer was coated with 5000 ppm Irganox® 1010 by evaporating an acetone slurry and drying in a vacuum oven. The polymer was pressed at 290°C into a transparent, gray-brown, tough film. DSC (25 to 330°C, 10°C/min, second

heat):  $T_g = 101^\circ\text{C}$ ,  $T_m$  (onset to end) = 161 to  $258^\circ\text{C}$ ,  
heat of fusion = 22 J/g.

Example 446

The complex  $[(2,4,6\text{-MePh})_2\text{DABAn}]\text{NiBr}_2$  was weighed  
5 (32 mg, 0.050 mmol) into a glass vial inside a dry box. Cyclopentene was added (6.81 g, 2000 equivalents per Ni; treated with 5 Å molecular sieves, and distilled from Na and  $\text{Ph}_3\text{CH}$ ), and the vial was cooled to  $<0^\circ\text{C}$ . A  
10 solution of  $\text{EtAlCl}_2\text{-}i\text{-Et}_2\text{AlCl}$  in toluene (1.9 mL, 0.91 M, 68 equivalents Al per Ni) was added with stirring to give a homogeneous solution. After 5 days, the solids were collected by vacuum filtration, washed several times on the filter with ether and cyclohexane, and dried in a vacuum oven to give 2.421 g polymer (711  
15 turnovers/Ni). The polymer was coated with 5000 ppm Irganox<sup>®</sup> 1010 by evaporating an acetone slurry and drying in a vacuum oven. The polymer was pressed at  $290^\circ\text{C}$  into a transparent, brown, tough film. DSC (25 to  $330^\circ\text{C}$ ,  $10^\circ\text{C}/\text{min}$ , second heat):  $T_g = 103^\circ\text{C}$ ,  $T_m$  (onset  
20 to end) = 178 to  $272^\circ\text{C}$ , heat of fusion = 22 J/g.

Example 447

The complex  $[(2,4,6\text{-MePh})_2\text{DABAn}]\text{NiBr}_2$  was weighed (128 mg, 0.202 mmol) into a glass bottle inside a dry box. Cyclopentene was added (27.1 g, 2000 equivalents  
25 per Ni; treated with polyphosphoric acid, and distilled from Na). A solution of  $\text{EtAlCl}_2$  in hexane (6.8 mL, 1.0 M, 34 equivalents Al per Ni) was added with stirring to give a homogeneous solution. After 1 day, additional cyclopentene was added (58 g, 6200 total equivalents  
30 per Ni) to the bottle containing a heavy slurry. After 5 days, the solids were slurried with ether, collected by vacuum filtration, washed several times with ether and cyclohexane on the filter, and dried in a vacuum oven to give 36.584 g polymer (2660 turnovers/Ni). The  
35 polymer was washed with 50:50 aqueous  $\text{HCl}/\text{MeOH}$ , followed by several washings with 50:50  $\text{H}_2\text{O}/\text{MeOH}$ , and dried in a vacuum oven. A fine powder sample was obtained using a 60 mesh screen, and coated with 5000

ppm Irganox® 1010 by evaporating an acetone slurry and drying in a vacuum oven. The fine powder was pressed at 290°C into a transparent, pale brown, tough film. TGA (25 to 700°C, 10°C/min, nitrogen):  $T_d$  (onset to end) = 478 to 510°C, 99.28 % weight loss. DSC (25 to 330°C, 10°C/min, second heat):  $T_g$  = 101°C,  $T_m$  (onset to end) = 174 to 279°C, heat of fusion = 25 J/g. DSC (330 to 25°C, 10 °C/min, first cool):  $T_c$  (onset to end) = 247 to 142°C, heat of fusion = 28 J/g;  $T_c$  (peak) = 223°C. DSC isothermal crystallizations were performed by heating samples to 330°C followed by rapid cooling to the specified temperatures, °C, and measuring the exotherm half-times (min): 200 (1.55), 210 (1.57), 220 (1.43), 225 (< 1.4), 230 (1.45), 240 (1.88), 245 (1.62). DSC thermal fractionation was performed by heating a sample to 330°C followed by stepwise isothermal equilibration at the specified temperatures, °C, and times (hr): 290 (10), 280 (10), 270 (10), 260 (10), 250 (10), 240 (8), 230 (8), 220 (8), 210 (8), 200 (6), 190 (6), 180 (6), 170 (6), 160 (4), 150 (4), 140 (4), 130 (3), 120 (3), 110 (3). DSC (25 to 330°C, 10°C/min, thermal fractionation sample):  $T_g$  = 100°C;  $T_m$ , °C (heat of fusion, J/g) = 128 (0.4), 139 (0.8), 146 (1.1), 156 (1.5), 166 (1.9), 176 (2.1), 187 (2.6), 197 (3.0), 207 (3.2), 216 (3.2), 226 (3.4), 237 (3.6), 248 (3.7), 258 (2.3), 269 (1.2), 279 (0.5), 283 (0.1); total heat of fusion = 34.6 J/g. DMA (-100 to 200°C, 1, 2, 3, 5, 10 Hz; pressed film): modulus (-100 °C) = 2500 MPa,  $\gamma$  relaxation = -67 to -70°C (activation energy = 11 kcal/mol), modulus (25°C) = 1600 MPa,  $\alpha$  relaxation ( $T_g$ ) = 109 to 110°C (activation energy = 139 kcal/mol).

#### Example 448

The complex  $[(2,4,6\text{-MePh})_2\text{DABAN}]\text{NiBr}_2$  was weighed (32 mg, 0.050 mmol) into a glass bottle inside a dry box. Cyclopentene was added (34.1 g, 10,000 equivalents per Ni; high-purity synthetic material distilled from Na), and the vial was cooled to <0°C. A

solution of MMAO in heptane (2.7 mL, 1.95 M Al, 100 equivalents Al per Ni) was added with stirring to give a homogeneous solution. After 3 days, a copious precipitate had formed. After 7 days, the reaction was  
5 quenched with 20 mL MeOH and 2 mL acetylacetone. The solids were washed several times with 3 mL aqueous HCl in 30 mL MeOH by decanting the free liquids. The solids were collected by vacuum filtration, washed several times on the filter with methanol, and dried in  
10 a vacuum oven to give 14.365 g polymer (4200 turnovers/Ni). The polymer was coated with 5000 ppm Irganox® 1010 by evaporating an acetone slurry and drying in a vacuum oven. The polymer was pressed at 290°C into a transparent, colorless, tough film. DSC  
15 (0 to 320°C, 20°C/min, second heat):  $T_g = 95^\circ\text{C}$ ,  $T_m$  (onset to end) = 175 to 287°C, heat of fusion = 20 J/g.

Example 449

The complex  $[(2,4,6\text{-MePh})_2\text{DABAN}]\text{NiBr}_2$  was weighed (32 mg, 0.050 mmol) into a glass bottle inside a dry  
20 box. Cyclopentene was added (34.1 g, 10,000 equivalents per Ni; high-purity synthetic material distilled from Na), and the vial was cooled to  $<0^\circ\text{C}$ . A solution of  $\text{EtAlCl}_2 \cdot \text{Et}_2\text{AlCl}$  in toluene (2.8 mL, 0.91 M, 100 equivalents Al per Ni) was added with stirring to  
25 give a homogeneous solution. After 3 days, a precipitate had formed. After 7 days, the reaction was quenched with 20 mL MeOH and 2 mL acetylacetone. The solids were washed several times with 3 mL aqueous HCl in 30 mL MeOH by decanting the free liquids. The  
30 solids were collected by vacuum filtration, washed several times on the filter with methanol, and dried in a vacuum oven to give 7.254 g polymer (2113 turnovers/Ni). The polymer was coated with 5000 ppm Irganox® 1010 by evaporating an acetone slurry and  
35 drying in a vacuum oven. The polymer was pressed at 290°C into a transparent, colorless, tough film. DSC (0 to 320°C, 20°C/min, second heat):  $T_g = 94^\circ\text{C}$ ,  $T_m$  (onset to end) = 189 to 274°C, heat of fusion = 18 J/g.



Example 450

Bis(benzonitrile)palladium dichloride (0.385 g, 1.00 mmol) and (2,6-iPrPh)<sub>2</sub>DABMe<sub>2</sub> (0.405 g, 1.00 mmol) were weighed into a glass vial inside a dry box.

5 Dichloromethane (8 mL) was added to give a dark orange solution. Upon standing, the solution gradually lightened in color. Cyclohexane was added to precipitate an orange solid. The solids were collected by vacuum filtration, washed several times with

10 cyclohexane, and dried under vacuum to give 0.463 g (80 %) of the complex [(2,6-iPrPh)<sub>2</sub>DABMe<sub>2</sub>]PdCl<sub>2</sub>. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>, referenced to solvent peak at 5.32 ppm): 1.19 (d, 12H, CH<sub>3</sub>-CHAr-CH<sub>3</sub>), 1.45 (d, 12H, CH<sub>3</sub>-CHAr-CH<sub>3</sub>), 2.07 (s, 6H, (CH<sub>3</sub>-C=N-Ar), 3.07 (m, 4H, (CH<sub>3</sub>)<sub>2</sub>-CH-Ar), 7.27 (d, 4H, meta ArH), 7.38 (t, 2H, para ArH).

Example 451

A sample of polycyclopentene prepared in a similar fashion to Example 317 gave a transparent, brown, tough

20 film when pressed at 290°C. DSC (25 to 330°C, 10°C/min, second heat): T<sub>g</sub> = 98°C, T<sub>m</sub> (onset to end) = 174 to 284 °C, heat of fusion = 26 J/g. A 5 g sample that was molded at 280°C into a test specimen suitable for an apparatus that measures the response to changes in

25 pressure, volume and temperature, and the data output was used to calculate the following physical properties. Specific gravity, g/cm<sup>3</sup>, at temperature (°C): 1.033 (30), 1.010 (110°C), 0.887 (280), 0.853 (350). Bulk compression modulus, MPa, at temperature

30 (°C): 3500 (30), 2300 (110), 1500 (170). The coefficient of linear thermal expansion was 0.00009 °C<sup>-1</sup> between 30 and 110°C.

Example 452

A solution of [(2,6-i-PrPh)<sub>2</sub>DABMe<sub>2</sub>]PdCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C(O)OCH<sub>3</sub>}<sup>+</sup>SbF<sub>6</sub><sup>-</sup> (1.703 g) in 1.5 L CH<sub>2</sub>Cl<sub>2</sub>

35 was transferred under nitrogen to a nitrogen purged 1 gallon Hastalloy® autoclave. The autoclave was charged with 300 g of propylene and stirred for 24 h

while maintaining the temperature at 25°C. The pressure was then vented. The polymer product was floating on the solvent. Most of the solvent was removed in vacuo, and the polymer was dissolved in minimal  $\text{CHCl}_3$  and then reprecipitated by addition of excess acetone. The polymer was dried in vacuo at 60°C for three days to give 271 g of green rubber. Quantitative  $^{13}\text{C}$  NMR analysis, branching per 1000  $\text{CH}_2$ : Total methyls (365),  $\geq$ Butyl and end of chains (8),  $\text{CHCH}_2\text{CH}(\text{CH}_3)_2$  (31),  $-(\text{CH}_2)_n\text{CH}(\text{CH}_3)_2$   $n \geq 2$  (25). Based on the total methyls, the fraction of 1,3-enchainment is 38%. Analysis of backbone carbons (per 1000  $\text{CH}_2$ ):  $\delta^+$  (138),  $\delta^+/\gamma$  (1.36).

Listed below are the  $^{13}\text{C}$  NMR data upon which the above analysis is based.

 $^{13}\text{C}$  NMR data

TCB, 120°C, 0.05M CrAcAc

Freq ppm	Intensity	
47.1728	14.6401	
46.7692	9.89618	
46.3285	13.3791	
45.8719	7.94399	
45.4684	11.1421	
45.2719	7.80142	
44.4754	7.11855	
39.1923	29.1488	
38.2791	14.2142	
38.1304	18.7602	
37.9074	14.9366	
37.6631	15.0761	
37.2809	39.5816	
35.5074	8.29039	
34.865	9.75536	
34.5889	14.9541	
34.2915	24.0579	
33.2455	9.86797	
32.9747	19.2516	
30.6013	52.6926	
30.134	55.0735	$\gamma$
30.0066	25.1831	$\gamma$
29.7518	144.066	$\delta^+$
29.3217	12.2121	$3B_4$
28.2013	51.5842	
27.9783	39.5566	
27.5376	33.189	
27.373	35.5457	
27.1659	47.0796	
27.0438	42.1247	

25.6315	21.6632	terminal methine of XXVIII
23.3589	15.3063	Methyl of XXVIII and XXIX, 2B <sub>4</sub> , 2B <sub>5</sub> +, 2EOC
23.0722	18.4837	Methyl of XXVIII and XXIX, 2B <sub>4</sub> , 2B <sub>5</sub> +, 2EOC
22.5306	77.0243	Methyl of XXVIII and XXIX, 2B <sub>4</sub> , 2B <sub>5</sub> +, 2EOC
21.1129	7.78367	
20.5554	26.9634	1B <sub>1</sub>
20.4386	30.3105	1B <sub>1</sub>
20.0085	22.478	1B <sub>1</sub>
19.743	46.6467	1B <sub>1</sub>
13.8812	9.03898	1B <sub>4</sub> +, 1EOC

Example 453

A 250 mL Schlenk flask was charged with 10 mg of [(2,6-i-PrPh)<sub>2</sub>DABH<sub>2</sub>]<sub>2</sub>NiBr<sub>2</sub> (1.7x10<sup>-5</sup> mol), and 75 mL of dry toluene. The flask was cooled to 0°C and filled with propylene (1 atm) before addition of 1.5 mL of a 10% MAO solution in toluene. After 45 min, acetone and water were added to quench the reaction. Solid polypropylene was recovered from the flask and washed with 6 M HCl, H<sub>2</sub>O, and acetone. The resulting polymer was dried under high vacuum overnight to yield 1.2 g (2300 TO/h) polypropylene. Differential scanning calorimetry : T<sub>g</sub> = -19°C. GPC (trichlorobenzene, 135°C, polystyrene reference): Mn = 32,500; Mw = 60,600; Mw/Mn = 1.86. Quantitative <sup>13</sup>C NMR analysis, branching per 1000 CH<sub>2</sub>: Total methyls (813). Based on the total methyls, the fraction of 1,3-enchainment is 7%. Analysis of backbone carbons (per 1000 CH<sub>2</sub>): δ<sup>+</sup> (3), δ<sup>+</sup>/γ (0.4).

Listed below are the <sup>13</sup>C NMR data upon which the above analysis is based.

<sup>13</sup>C NMR data

TCB, 120C, 0.05M CrAcAc	
Freq ppm	Intensity
47.194	18.27
46.9922	21.3352
46.8276	35.7365
46.2011	27.2778
45.4153	8.55108
43.5356	2.71929
42.925	3.37998

41.5551	2.63256
38.826	3.03899
38.4012	10.2858
38.0561	8.50185
37.626	7.10732
37.4879	6.55335
37.2755	9.25058
36.1021	4.48005
35.3057	14.5319
34.4986	11.1193
33.219	9.43548
32.9375	4.94953
32.242	3.16177
30.8349	24.1766
30.5217	19.8151
30.0916	3.70031
28.1111	144
27.5217	13.9133
27.1394	3.83857
24.5005	6.94946
21.0439	5.25857
20.5342	40.8641
20.0191	60.4325
19.8758	63.0429
16.9236	6.47935
16.3926	5.92056
14.9006	10.6275
14.513	3.39891

Example 454

Preparation of (2-t-BuPh)<sub>2</sub>DABAn. A Schlenk tube was charged with 2-t-butylaniline (3.00 mL, 19.2 mmol) and acenaphthenequinone (1.71 g, 9.39 mmol). The reagents were partially dissolved in 50 mL of methanol (acenaphthenequinone was not completely soluble) and 1-2 mL of formic acid was added. An orange solid formed and was collected via filtration after stirring overnight. The solid was crystallized from CH<sub>2</sub>Cl<sub>2</sub> (3.51 g, 84.1%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz) δ 7.85 (d, 2H, J = 8.0 Hz, BIAN: H<sub>P</sub>), 7.52 (m, 2H, Ar: H<sub>m</sub>), 7.35 (dd, 2H, J = 8.0, 7.3 Hz, BIAN: H<sub>m</sub>), 7.21 (m, 4H, Ar: H<sub>m</sub> and H<sub>P</sub>), 6.92 (m, 2H, Ar: H<sub>O</sub>), 6.81 (d, 2H, J = 6.9 Hz, BIAN: H<sub>O</sub>), 1.38 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>).

Example 455

Preparation of (2,5-t-BuPh)<sub>2</sub>DABAn. A Schlenk tube was charged with 2,5-di-t-butylaniline (2.00 g, 9.74 mmol) and acenaphthenequinone (0.88 g, 4.8 mmol). The

reagents were partially dissolved in 50 mL of methanol (acenaphthenequinone was not completely soluble) and 1-2 mL of formic acid was added. A solid was collected via filtration after stirring overnight. Attempted  
5 crystallization from ether and from  $\text{CH}_2\text{Cl}_2$  yielded an orange/yellow powder (1.75 g, 66%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 250 MHz)  $\delta$  7.85 (d, 2H,  $J = 8.1$  Hz, BIAN:  $\text{H}_\text{p}$ ), 7.44 (d, 2H,  $J = 8.4$  Hz, Ar:  $\text{H}_\text{m}$ ), 7.33 (dd, 2H,  $J = 8.4$ , 7.3 Hz, BIAN:  $\text{H}_\text{m}$ ), 7.20 (dd, 2H,  $J = 8.1$ , 2.2 Hz, Ar:  $\text{H}_\text{p}$ ), 6.99  
10 (d, 2H,  $J = 2.2$  Hz, Ar:  $\text{H}_\text{o}$ ), 6.86 (d, 2H,  $J = 7.0$  Hz, BIAN:  $\text{H}_\text{o}$ ), 1.37, 1.27 (s, 18H each,  $\text{C}(\text{CH}_3)_3$ ).

#### Example 456

Preparation of  $[(2\text{-t-BuPh})_2\text{DABAN}]\text{NiBr}_2$ . A Schlenk tube was charged with 0.202 g (0.454 mmol) of (2-t-BuPh) $_2$ DABAN, which was then dissolved in 15 mL of  
15  $\text{CH}_2\text{Cl}_2$ . This solution was cannulated onto a suspension of (DME) $\text{NiBr}_2$  (0.135 g, 0.437 mmol) in 10 mL of  $\text{CH}_2\text{Cl}_2$ . The reaction mixture was allowed to stir overnight resulting in a deep red solution. The solution was  
20 filtered and the solvent evaporated under vacuum. The residue was washed with ether (2x10 mL) and an orange/rust solid was isolated and dried under vacuum (0.18g, 62%).

#### Example 457

25 Preparation of  $[(2,5\text{-t-BuPh})_2\text{DABAN}]\text{NiBr}_2$ . A Schlenk tube was charged with 0.559 g (1.00 mmol) of (2,5-t-BuPh) $_2$ DABAN, 0.310 g (1.00 mmol) of (DME) $\text{NiBr}_2$  and 35 mL of  $\text{CH}_2\text{Cl}_2$ . The reaction mixture was allowed to stir overnight. The solution was filtered and the  
30 solvent evaporated under vacuum. The residue was washed with ether and resulted in an orange solid which was dried under vacuum (0.64 g, 83%).

#### Example 458

Preparation of highly chain-straightened polypropylene with a low  $T_g$ . The complex  $[(2\text{-t-BuPh})_2\text{DABAN}]\text{NiBr}_2$   
35 (0.0133g,  $2.0 \times 10^{-5}$  mol) was placed into a flame-dried 250 mL Schlenk flask which was then evacuated and back-filled with propylene. Freshly distilled toluene (100

mL) was added via syringe and the resulting solution was stirred in a water bath at room temperature. Polymerization was initiated by addition of methylaluminoxane (MAO; 1.5 mL 10% soln in toluene) and  
5 a propylene atmosphere was maintained throughout the course of the reaction. The reaction mixture was stirred for two hours at constant temperature followed by quenching with 6M HCl. Polymer was precipitated from the resulting solution with acetone, collected,  
10 washed with water and acetone, and dried under vacuum. Yield = 1.41 g. DSC:  $T_g$   $-53.6^\circ\text{C}$ ,  $T_m$   $-20.4^\circ\text{C}$  (apparent  $T_m$  is a small shoulder on the  $T_g$ ). Quantitative  $^{13}\text{C}$  NMR analysis, branching per 1000  $\text{CH}_2$ : Total methyls (226),  $\geq$ Butyl and end of chains (8.5),  $\text{CHCH}_2\text{CH}(\text{CH}_3)_2$  (2.3), -  
15  $(\text{CH}_2)_n\text{CH}(\text{CH}_3)_2$   $n \geq 2$  (12.1). Based on the total methyls, the fraction of 1,3-enchainment is 53%. Analysis of backbone carbons (per 1000  $\text{CH}_2$ ):  $\delta^+$  (254),  $\delta^+/\gamma$  (1.96).

#### Example 459

20 Preparation of highly chain-straightened polypropylene with a low  $T_g$ . The complex  $[(2,5\text{-}t\text{-BuPh})_2\text{DABAn}]\text{NiBr}_2$  ( $0.0155\text{g}$ ,  $2.0 \times 10^{-5}$  mol) was placed into a flame-dried 250 mL Schlenk flask which was then evacuated and back-filled with propylene. Freshly  
25 distilled toluene (100 mL) was added via syringe and the resulting solution was stirred in a water bath at room temperature. Polymerization was initiated by addition of 1.5 mL of a 10% MAO solution in toluene, and a propylene atmosphere was maintained throughout  
30 the course of the reaction. The reaction mixture was stirred for two hours at constant temperature followed by quenching with 6M HCl. Polymer was precipitated from the resulting solution with acetone, collected, washed with water and acetone, and dried under vacuum.  
35 Yield = 0.75 g. DSC:  $T_g$   $-53.0^\circ\text{C}$ ,  $T_m$  none observed. Quantitative  $^{13}\text{C}$  NMR analysis, branching per 1000  $\text{CH}_2$ : Total methyls (307),  $\geq$  Butyl and end of chains (11.2),  $-\text{CHCH}_2\text{CH}(\text{CH}_3)_2$  (11.5),  $-(\text{CH}_2)_n\text{CH}(\text{CH}_3)_2$ ,  $n \geq 2$  (5.9). Based

on the total methyls, the fraction of 1,3-enchainment is 43%.

Listed below are the  $^{13}\text{C}$  NMR data upon which the above analysis is based.

5

 $^{13}\text{C}$  NMR data

TCB, 120C, 0.05M CrAcAc		
Freq ppm	Intensity	
46.3126	6.77995	
46.079	6.56802	
45.463	7.82411	
45.2453	6.98049	
39.1764	8.95757	
38.4384	5.42739	
38.1145	20.5702	
37.8755	18.8654	
37.626	19.2917	
37.2702	128.202	
35.0773	6.30042	
34.5304	19.5098	
34.2543	38.6071	
33.7818	4.3205	
33.2986	16.3395	
32.9588	72.1002	
31.934	10.626	
31.419	5.57124	
30.5907	41.727	
30.1287	134.312	$\gamma$
29.7518	351.463	$\delta^+$
29.3217	9.58971	
28.1589	21.1043	
27.9677	17.7659	
27.5589	44.1485	
27.3783	25.0491	
27.1766	119.562	
27.0226	52.4586	
~25.6		terminal methine of XXVIII
24.5908	8.69462	
24.4315	9.27804	
22.5253	30.7474	region of methyls of XXVIII and XXIX, $2\text{B}_4^+$ , 2EOC
20.4333	20.0121	$1\text{B}_1$
19.7271	103.079	$1\text{B}_1$
14.7679	5.0022	
14.4068	4.56246	
13.8812	12.3077	$1\text{B}_4^+$ , 1EOC

Example 460

Preparation of highly chain-straightened poly-1-hexene with a high  $T_m$ . A flame-dried 250 mL Schlenk flask under a nitrogen atmosphere was charged with 40 mL of freshly distilled toluene, 0.0133 g of [(2-t-

BuPh)<sub>2</sub>DABAn]NiBr<sub>2</sub> ( $2.0 \times 10^{-5}$  mol), 5.0 mL of 1-hexene, and 55 mL more toluene (100 mL total volume of liquid). Polymerization was initiated by addition of 2.0 mL of MAO (10% solution in toluene). The reaction mixture  
5 was stirred for 11.5 hours at room temperature followed by quenching with 6M HCl. Polymer was precipitated from the resulting solution with acetone, collected via filtration, washed with water and acetone, and dried under vacuum. Yield = 1.84 g. DSC: T<sub>g</sub> -44.8°C, T<sub>m</sub>  
10 46.0°C.

#### Example 461

Preparation of highly chain-straightened poly-1-hexene with a high T<sub>m</sub>. A flame-dried 250 mL Schlenk flask under a nitrogen atmosphere was charged with 40  
15 mL of freshly distilled toluene, 0.0155g of [(2,5-t-BuPh)<sub>2</sub>DABAn]NiBr<sub>2</sub> ( $2.0 \times 10^{-5}$  mol), 5.0 mL of 1-hexene, and 55 mL more toluene (100 mL total volume of liquid). Polymerization was initiated by addition of 2.0 mL of MAO (10% solution in toluene). The reaction mixture  
20 was stirred for 11.5 hours at room temperature followed by quenching with 6M HCl. Polymer was precipitated from the resulting solution with acetone, collected via filtration, washed with water and acetone, and dried under vacuum. Yield = 1.07 g. DSC: T<sub>g</sub> -54.7°C, T<sub>m</sub>  
25 12.5°C.

#### Example 462

Preparation of [(2-t-BuPh)<sub>2</sub>DABAn]PdMe<sub>2</sub> from (1,5-cyclooctadiene)PdMe<sub>2</sub>. The Pd(II) precursor (1,5-cyclooctadiene)PdMe<sub>2</sub> ((COD)PdMe<sub>2</sub>) was prepared  
30 according reported procedures (Rudler-Chauvin, M.; Rudler, H. J. *Organomet. Chem.*, 1977, 134, 115.) and was handled using Schlenk techniques at temperatures of -10°C or below. A flame-dried Schlenk tube was charged with 0.056 g (0.229 mmol) of (COD)PdMe<sub>2</sub> and cooled to -  
35 40°C in a dry ice/isopropanol bath. The solid was dissolved in 10 mL of ether, and the diimine (2-t-BuPh)<sub>2</sub>DABAn (0.106 g, 0.238 mmol) was cannulated onto the stirring solution as a slurry in 15 mL of ether.



The reaction was warmed to 0 °C and stirring was continued for two hours. The reaction flask was stored at -30°C for several days and resulted in the formation of a green precipitate which was isolated via  
5 filtration. The supernatant was pumped dry under high vacuum and also resulted in a green solid. Both solids were determined to be [(2-t-BuPh)<sub>2</sub>DABAn]PdMe<sub>2</sub> by <sup>1</sup>H NMR spectroscopy. Isolated yield = 0.083 g (0.143 mmol, 62.4%).

10

Example 463

Preparation of [(2,5-t-BuPh)<sub>2</sub>DABAn]PdMe<sub>2</sub> from (1,5-cyclooctadiene)PdMe<sub>2</sub>. The Pd(II) precursor (1,5-cyclooctadiene)PdMe<sub>2</sub> ((COD)PdMe<sub>2</sub>) was prepared according reported procedures (Rudler-Chauvin, M.;  
15 Rudler, H. J. *Organomet. Chem.*, 1977, 134, 115.) and was handled using Schlenk techniques at temperatures of -10°C or below. A flame-dried Schlenk tube was charged with 0.102 g (0.417 mmol) of (COD)PdMe<sub>2</sub> and cooled to -30°C in a dry ice/isopropanol bath. The solid was  
20 dissolved in 10 mL of ether, and the diimine (2,5-t-BuPh)<sub>2</sub>DABAn (0.234 g, 0.420 mmol) was cannulated onto the stirring solution as a slurry in 40 mL of ether. The reaction was warmed to 0°C and stirring was continued for four hours. The reaction flask was  
25 stored at -30°C overnight. The resulting dark green solution was filtered and the solvent was pulled off under high vacuum to give a dark green powder. Analysis by <sup>1</sup>H NMR spectroscopy showed the solid to be consistent with the desired product, [(2,5-t-BuPh)<sub>2</sub>DABAn]PdMe<sub>2</sub>. Yield = 0.256 g (0.370 mmol, 88.7%).  
30

Example 464

In a dry box, polymer from Example 469 (0.57 g), THF (10.10 g) and acetic anhydride (0.65 g) were placed  
35 in a 20 mL vial equipped with a stirring bar. After one hour at room temperature, the vial was removed from the dry box and the polymerization terminated by the addition of THF, water and ether. The organic phase

was separated, washed with water (2x), dried over anhydrous sodium sulfate, concentrated at reduced pressure and then dried under vacuum, affording 4.44 g of polymer. GPC analysis (PS STD.): Mn = 17600, Mw =  
5 26000, PD = 1.48.

Example 465

Preparation of  $\text{CH}_2=\text{CH}(\text{CH}_2)_2\text{CHICH}_2(\text{CF}_2)_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$

A mixture of 72 g of hexadiene, 127.8 g of  $\text{ICF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ , 7.0 g of Cu powder and 180 mL of  
10 hexane was stirred at 90°C overnight. Solids were removed by filtration and washed with hexane. After removal of volatiles, residue was distilled to give 115.3 g of product, bp 80°C/210 Pa.  $^{19}\text{F}$  NMR: +45 (t, J = 6.0 Hz, 1F), -82.7 (m, 2F), -88.1 (dt, J = 42.5 Hz, J =  
15 12.6 Hz, 1F), -88.7 (dt, J = 45.5 Hz, J = 12.6 Hz, 1F), -112.7 (m, 2F), -115.9 (ddd, J = 2662.2 Hz, J = 30.0 Hz, J = 8.2 Hz, 1F), -118.9 (ddd, J = 262.2 Hz, J = 26.8 Hz, J = 7.4 Hz, 1F).

Example 466

20 Preparation of  $\text{CH}_2=\text{CH}(\text{CH}_2)_4(\text{CF}_2)_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$

To a stirred solution of 100 g of  $\text{CH}_2=\text{CH}(\text{CH}_2)_2\text{CHICH}_2(\text{CF}_2)_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$  and 200 mL of ether was added 63 g of  $\text{Bu}_3\text{SnH}$  at room temperature. After the addition was complete, the reaction mixture was  
25 refluxed for 4 hours and then cooled with ice water. Excess of  $\text{Bu}_3\text{SnH}$  was destroyed by addition of iodine. After being diluted with 200 mL of ether, the reaction mixture was treated with a solution of 25 g of KF in 200 mL of water for 30 min. The solids were removed by  
30 filtration through a funnel with silica gel and washed with ether. The ether layer was separated and washed with water, aqueous NaCl solution and dried over  $\text{MgSO}_4$ . After removal of the ether, residue was distilled to give 54.7 g of product, bp 72°C/1.3 kPa, and 12.2 g of  
35 starting material.

$^{19}\text{F}$  NMR: +45 (m, 1F), -82.7 (m, 2F), -88.0 (m, 2F), -112.6 (m, 2F), -118.6 (t, J = 18.4 Hz, 2F).

Example 467

Preparation of  $\text{CH}_2=\text{CH}(\text{CH}_2)_4(\text{CF}_2)_4\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$

A mixture of 24 g of hexadiene, 53 g of  $\text{I}(\text{CF}_2)_4\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ , 3.0 g of Cu powder and 60 mL of hexane was stirred at 70°C overnight. Solids were removed by filtration and washed with hexane. After removal of volatiles, residue was distilled to give 115.3 g of adduct,  $\text{CH}_2=\text{CH}(\text{CH}_2)_2\text{CHICH}_2(\text{CF}_2)_4\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ , bp 74°C/9 Pa.  $^{19}\text{F}$  NMR: +45.5 (m, 1F), -82.4 (m, 2F), -83.5 (m, 2F), -112.2 (dm, J = 270 Hz, 1F), -112.6 (m, 2F), -115.2 (dm, J = 270 Hz, 1F), -124.3 (s, 2F), -125.5 (m, 2F).

To stirred solution of 47 g of  $\text{CH}_2=\text{CH}(\text{CH}_2)_2\text{CHICH}_2(\text{CF}_2)_4\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$  and 150 mL of ether was added 27 g of  $\text{Bu}_3\text{SnH}$  at room temperature. After the addition was complete, the reaction mixture was stirred overnight. Excess of  $\text{Bu}_3\text{SnH}$  was destroyed by addition of iodine. After being diluted with 150 mL of ether, the reaction mixture was treated with a solution of 20 g of KF in 100 mL of water for 30 min. The solids were removed by filtration through a funnel with silica gel and washed with ether. The ether layer was separated and washed with water, aqueous NaCl solution and dried over  $\text{MgSO}_4$ . After removal of the ether, residue was distilled to give 24.7 g of product, bp 103°C/1.3 kPa.  $^{19}\text{F}$  NMR: +45.4 (m, 1F), -82.4 (m, 2F), -83.5 (m, 2F), -112.6 (t, J = 2.6 Hz, 2F), -115.1 (t, J = 15 Hz, 2F), -124.3 (s, 2F), -125.7 (t, J = 14 Hz, 2F). HRMS: calcd for  $\text{C}_{12}\text{H}_{11}\text{F}_{13}\text{SO}_3$ : 482.0221. Found: 482.0266.

Example 468

## Hydrolysis of Copolymer

Copolymer containing 8.5 mol% of comonomer (1.5 g) was dissolved in 30 mL of THF at room temperature. KOH (0.5 g) in 5 mL of ethanol and 3 mL of water was added and the resulting mixture was stirred at room temperature for six hours. After removal of the solvent, residue was treated with diluted HCl for 70 hours and then filtered to give solids which were

washed with water, HCl and dried under full vacuum at 70°C for two days to give 1.4 g solid.

Example 469

Hydrolysis of Copolymer

5 A mixture of 10.6 g of copolymer 5.0 g of KOH, 2 mL of water, 30 mL of ethanol and 30 mL of THF was stirred at room temperature overnight and at 60 to 70°C for 5 hours. After removal of a half of solvents, residue was treated with Conc. HCl to give rubbery  
10 material, which was poured into a blender and blended with water for 30 min. Filtration gave solids, which were washed with conc. HCl, and water and dried under vacuum at 60°C overnight to give 8.7 g of dark rubbery material.  $^{19}\text{F}$  NMR(THF): -82.8 (br, 2F), -88.5 (br, 2F),  
15 -118.3 (br, 2F), -118.5 (br, 2F).

Example 470

Hydrolysis of Homopolymer

A solution of 2.0 g of KOH in 25 mL of ethanol and 2 mL of water was added to a flask with 3.0 g of  
20 homopolymer. The resulting heterogeneous mixture was stirred at room temperature overnight and heated to 60°C for 2 hours. After removal of one-half of liquid, the reaction mixture treated with 40 mL of conc. HCl for 30 min. Filtration gave white solids which were  
25 washed with conc. HCl, and distilled water and dried under vacuum at 60-70°C for 24 hours to give 2.9 g of white powder.

Example 471

1-Octadecene (8 mL, 8 vol %) was added to a  
30 suspension of [(2,6-*i*-PrPh)<sub>2</sub>DABAn]NiBr<sub>2</sub> (12 mg,  $1.7 \times 10^{-5}$  mol) in 100 mL of dry toluene. The flask was cooled to -1°C using an Endocal® refrigerated circulating bath and 2.5 mL of a 7% MMAO solution in heptane was added. After stirring the reaction for 40 min, the flask was  
35 filled with propylene (1 atm) and stirred for 20 minutes. The propylene was removed in vacuo and the reaction allowed to continue for an additional 40 min. Acetone and water were added to quench the

polymerization and precipitate the polymer. The resulting triblock polymer was dried under high vacuum overnight to yield 650 mg of a rubbery solid. GPC (trichlorobenzene, 135 °C, polystyrene reference):  $M_n =$   
5 60,100;  $M_w = 65,500$ ;  $M_w/M_n = 1.09$ . DSC analysis: Two melt transitions were observed.  $T_m = 8^\circ\text{C}$  (32 J/g),  $T_m = 37^\circ\text{C}$  (6.5 J/g).  $^1\text{H-NMR}$  analysis ( $\text{CDCl}_3$ ): signals attributable to repeat units of propylene and 1-octadecene were observed.

10

Example 472Preparation of (2-*i*-Pr-6-MePh) $_2$ DABAn

A Schlenk tube was charged with 2-isopropyl-6-methylaniline (5.00 mL, 30.5 mmol) and acenaphthenequinone (2.64 g, 14.5 mmol). The reagents  
15 were partially dissolved in 50 mL of methanol (acenaphthenequinone was not completely soluble) and 1-2 mL of formic acid was added. An orange/yellow solid was collected via filtration after stirring overnight, and was washed with methanol and dried under vacuum.

20

Example 473Preparation of (2-*i*-Pr-6-MePh) $_2$ DABMe $_2$ 

A Schlenk tube was charged with 2-isopropyl-6-methylaniline (5.00 mL, 30.5 mmol) and 2,3-butanedione (1.31 mL, 14.9 mmol). Methanol (5 mL) and one drop of  
25 concentrated HCl were added and the mixture was heated to reflux with stirring for 30 minutes. The methanol and remaining dione were removed under vacuum to give a dark, oily residue. The oil was chromatographed on a silica gel column using 10% ethyl acetate: 90% hexane  
30 as the eluent. The fractions containing the pure diimine were combined and concentrated. The remaining solvents were removed under vacuum to give a pale yellow powder (0.9217 g, 17.75 %).

35

Example 474Preparation of [(2-*i*-Pr-6-MePh) $_2$ DABAn]NiBr $_2$ 

Under inert conditions, a flame-dried Schlenk tube was charged with 0.50 g (1.13 mmol) of (2-*i*-Pr-6-MePh) $_2$ DABAn, 0.34 g (1.10 mmol) of (DME)NiBr $_2$  and 25 mL

of CH<sub>2</sub>Cl<sub>2</sub>. The reaction mixture was allowed to stir overnight. The solution was filtered and the solvent removed under vacuum. The residue was washed with ether (4 x 10 mL) to give an orange/yellow powder which  
5 was dried under vacuum overnight (0.68 g, 94%).

Example 475

Preparation of [(2-*i*-Pr-6-MePh)<sub>2</sub>DABMe<sub>2</sub>]NiBr<sub>2</sub>

Under inert conditions, a flame-dried Schlenk tube was charged with 0.3040 g (0.8722 mmol) of (2-*i*-Pr-6-MePh)<sub>2</sub>DABMe<sub>2</sub>, 0.2640 g (0.8533 mmol) of (DME)NiBr<sub>2</sub> and  
10 25 mL of CH<sub>2</sub>Cl<sub>2</sub>. The reaction mixture was allowed to stir overnight. A solid was collected via filtration and washed with ether (2 x 10 mL). Upon sitting, more solid precipitated from the supernatant. This  
15 precipitate was isolated via filtration, washed with ether, and combined with the originally isolated product. The combined yellow/orange solids were dried under vacuum overnight (0.68 g, 94%).

Example 476

20 Under a nitrogen atmosphere, the complex [(2-*i*-Pr-6-MePh)<sub>2</sub>DABAn]NiBr<sub>2</sub> (0.0099 g, 1.5x10<sup>-5</sup> mol) was placed into a flame-dried 250 mL Schlenk flask which was then evacuated and back-filled with propylene. Freshly distilled toluene (100 mL) was added via syringe and  
25 the resulting solution was stirred for five minutes at room temperature. Polymerization was initiated with addition of methylaluminoxane (MAO; 1.5 mL 10% solution in toluene) and a propylene atmosphere was maintained throughout the course of the reaction. The reaction  
30 was stirred for two hours at constant temperature, at which point the polymerization was by quenched with 6M HCl. Polymer was precipitated from the resulting solution with acetone, washed with water and acetone, and dried under vacuum. Yield = 3.09 g. DSC: T<sub>g</sub> -  
35 31.2°C. GPC: M<sub>n</sub> = 142,000; M<sub>w</sub> = 260,000; M<sub>w</sub>/M<sub>n</sub> = 1.83.

Example 477

Under a nitrogen atmosphere, the complex [(2-i-Pr-6-MePh)<sub>2</sub>DABMe<sub>2</sub>]NiBr<sub>2</sub> (0.0094 g, 1.5x10<sup>-5</sup> mol) was placed into a flame-dried 250 mL Schlenk flask which was then evacuated and back-filled with propylene. Freshly distilled toluene (100 mL) was added via syringe and the resulting solution was stirred for five min at room temperature. Polymerization was initiated with addition of methylaluminoxane (MAO; 1.5 mL 10% solution in toluene) and a propylene atmosphere was maintained throughout the course of the reaction. The reaction was stirred for two hours at constant temperature, at which point the polymerization was by quenched with 6M HCl. Polymer was precipitated from the resulting solution with acetone, washed with water and acetone, and dried under vacuum. Yield = 1.09 g. DSC: T<sub>g</sub> -36.1°C. GPC: M<sub>n</sub> = 95,300; M<sub>w</sub> = 141,000; M<sub>w</sub>/M<sub>n</sub> = 1.48.

Example 478

Under a nitrogen atmosphere, a flame-dried 250 mL Schlenk flask was charged with 40 mL of freshly distilled toluene, 0.0133 g (2.0x10<sup>-5</sup> mol) of [(2-i-Pr-6-MePh)<sub>2</sub>DABAn]NiBr<sub>2</sub>, 10.0 mL of 1-hexene, and 50 mL more toluene (100 mL total volume of liquid). The mixture was stirred in a room temperature water bath for 10 minutes and polymerization was initiated with addition of 2.0 mL of MAO (10% solution in toluene). The reaction mixture was stirred for one hour at room temperature and was quenched with 6M HCl. Polymer was precipitated from the resulting solution with acetone, collected via filtration, washed with water and acetone, and dried under vacuum. Yield = 3.23 g. DSC: T<sub>g</sub> -58.0°C, T<sub>m</sub> -16.5°C.

Example 479

Under a nitrogen atmosphere, a flame-dried 250 mL Schlenk flask was charged with 40 mL of freshly distilled toluene, 0.0125 g (2.0x10<sup>-5</sup> mol) of [(2-i-Pr-6-MePh)<sub>2</sub>DABMe<sub>2</sub>]NiBr<sub>2</sub>, 10.0 mL of 1-hexene, and 50 mL

more toluene (100 mL total volume of liquid). The mixture was stirred in a room temperature water bath for 10 min and polymerization was initiated with addition of 2.0 mL of MAO (10% solution in toluene).

- 5 The reaction mixture was stirred for 22 h at room temperature and was quenched with 6M HCl. Polymer was precipitated from the resulting solution with acetone, collected via filtration, washed with water and acetone, and dried under vacuum. Yield = 2.10 g. DSC:  
10  $T_g$   $-56.4^{\circ}\text{C}$ ,  $T_m$   $0.2^{\circ}\text{C}$ .

Example 480

- Under a nitrogen atmosphere, a flame-dried 250 mL Schlenk flask was charged with 40 mL of freshly distilled toluene,  $0.0133\text{ g}$  ( $2.0 \times 10^{-5}\text{ mol}$ ) of [(2-t-  
15 BuPh) $_2$ DABAn]NiBr $_2$ , 10.0 mL of 1-hexene, and 50 mL more toluene (100 mL total volume of liquid). The mixture was stirred in an isopropanol bath maintained at approximately  $-10$  to  $-12^{\circ}\text{C}$ , and polymerization was initiated with addition of 2.5 mL of MMAO (7.2%  
20 solution in heptane). The reaction mixture was stirred for two hours at constant temperature and was quenched with acetone/water/6M HCl. The mixture was added to acetone to precipitate the polymer. After settling overnight the polymer was collected via filtration,  
25 washed with water and acetone, and dried under vacuum. Yield = 0.35 g. DSC: (two broad melt transitions observed)  $T_m(1)$   $34.3^{\circ}\text{C}$ ,  $T_m(2)$   $66.4^{\circ}\text{C}$ . Based on the  $^1\text{H}$  NMR spectrum, the polymer contains 41 methyl branches/1000 carbons (theoretical = 55.5 Me/1000 C),  
30 indicating a high degree of chain straightening.

Example 481

- Under a nitrogen atmosphere, a flame-dried 250 mL Schlenk flask was charged with 25 mL of freshly distilled toluene,  $0.0133\text{ g}$  ( $2.0 \times 10^{-5}\text{ mol}$ ) of [(2-t-  
35 BuPh) $_2$ DABAn]NiBr $_2$ , 63 mL more toluene, and 12.0 mL of 1-octadecene (100 mL total volume of liquid). The flask was cooled to  $-10^{\circ}\text{C}$  in a  $\text{CO}_2$ /isopropanol bath and stirred at this temperature for several minutes. The



temperature was maintained at approximately  $-10^{\circ}\text{C}$  throughout the reaction by continually adding dry ice as needed. Polymerization of 1-octadecene was initiated with addition of 2.5 mL of MMAO (7.2% solution in heptane). At 2 h, 10 min the reaction flask was twice evacuated and back-filled with propylene. The polymerization was stirred under one atmosphere of propylene for 20 min. The propylene was removed by repeatedly evacuating the flask and back-filling with argon until propylene evolution from the solution was no longer apparent. The polymerization was allowed to continue stirring in the presence of the remaining 1-octadecene until a total elapsed time of five hours was reached. The reaction was quenched with acetone/water/6M HCl. Polymer was precipitated in methanol/acetone, collected via filtration, washed with water and acetone, and dried under vacuum. Yield = 1.03 g. DSC:  $T_g$   $8.0^{\circ}\text{C}$ ,  $T_m$   $53.3^{\circ}\text{C}$ . GPC:  $M_n = 55,500$ ;  $M_w = 68,600$ ;  $M_w/M_n = 1.24$ . It is believed a block copolymer was formed.

#### Example 482

Preparation of  $[(2\text{-}t\text{-BuPh})_2\text{DABAn}]\text{PdMe}(\text{Et}_2\text{O})\text{BAF}^-$

Under inert conditions, a flame-dried Schlenk tube was charged with 0.1978 g ( $3.404 \times 10^{-4}$  mol) of  $[(2\text{-}t\text{-BuPh})_2\text{DABAn}]\text{PdMe}_2$  and 0.3451 g ( $3.408 \times 10^{-4}$  mol) of  $\text{H}^+(\text{Et}_2\text{O})_2\text{BAF}^-$ . The Schlenk tube was cooled to  $-78^{\circ}\text{C}$  and 10 mL of ether was added. The Schlenk tube was transferred to an ice water bath and the reaction was stirred until the solids were dissolved and the color of the solution became deep red. The ether was then removed under vacuum to give a red, glassy solid that was crushed into a powder (yield was quantitative).

#### Example 483

Preparation of  $[(2,5\text{-}t\text{-BuPh})_2\text{DABAn}]\text{PdMe}(\text{Et}_2\text{O})\text{BAF}^-$

Following the procedure of Example 482, a red solid with the structure  $[(2,5\text{-}t\text{-BuPh})_2\text{DABAn}]\text{PdMe}(\text{Et}_2\text{O})\text{BAF}^-$  was obtained (quantitative yield).

Example 484

Preparation of [(2-t-BuPh)<sub>2</sub>DABMe<sub>2</sub>]PdMe(NCMe)BAF<sup>-</sup>

Under inert conditions, a flame-dried Schlenk tube was charged with 0.1002 g (0.378 mmol) of (COD)PdMeCl and 0.3348 g (0.378 mmol) of NaBAF. The Schlenk tube was cooled to -30°C and 25 mL of CH<sub>2</sub>Cl<sub>2</sub> and 0.10 mL of NCMe were added via syringe. The reaction was stirred for two h at -20 to -30°C. The resulting colorless solution was filtered into another cooled Schlenk tube, 20 mL of hexane was added, and the solvents were removed under vacuum to give a white powder [isolated (COD)PdMe(NCMe)BAF<sup>-</sup>]. This cationic precursor was combined with 0.138 g (0.396 mmol) of (2-t-BuPh)<sub>2</sub>DABMe<sub>2</sub> in 50 mL of NCMe. The reaction mixture was stirred overnight at room temperature. The solution was filtered and extracted with hexane (3 x 10 mL), and the solvents were removed under vacuum. The resulting yellow oil was dissolved in CH<sub>2</sub>Cl<sub>2</sub>/hexane and the solvents were removed under vacuum to give a glassy solid that was crushed into a powder. Two isomers were observed in solution by <sup>1</sup>H NMR spectroscopy. These two isomers arise from the coordination of the unsymmetrically substituted ligand in either the cis or trans fashion in regard to the t-butyl groups relative to the square plane of the complex.

Example 485

Polymerization of ethylene with [(2-t-BuPh)<sub>2</sub>DABAn]PdMe(Et<sub>2</sub>O)BAF<sup>-</sup>

A flame-dried 250 mL Schlenk flask was charged with 0.1505 g (1.001x10<sup>-4</sup> mol) of [(2-t-BuPh)<sub>2</sub>DABAn]PdMe(Et<sub>2</sub>O)BAF<sup>-</sup> in the glove box. The flask was twice evacuated and back-filled with ethylene and then cooled to -60°C. The solid was dissolved in 100 mL of CH<sub>2</sub>Cl<sub>2</sub> and the flask was allowed to warm to room temperature with stirring under an atmosphere of ethylene. After stirring for 23 h the polymerization was quenched with methanol. The solvent was removed under reduced pressure and the polymer was dissolved in

petroleum ether and filtered through silica gel. The filtrate was concentrated and the remaining solvent was removed under vacuum to give a clear, colorless, viscous liquid. Yield = 0.2824 g.  $^1\text{H}$  NMR analysis:

5 125 Me/1000  $\text{CH}_2$ .

Example 486

A flame-dried 250 mL Schlenk flask was charged with 0.1621 g ( $1.003 \times 10^{-4}$  mol) of [(2,5-t-BuPh) $_2$ DABAn]PdMe(Et $_2$ O)BAF $^-$  in the glove box. The flask  
10 was twice evacuated and back-filled with ethylene and then cooled to  $-60^\circ\text{C}$ . The solid was dissolved in 100 mL of  $\text{CH}_2\text{Cl}_2$  and the flask was allowed to warm to room temperature with stirring under an atmosphere of ethylene. After stirring for 23 h the polymerization  
15 was quenched with methanol. The solvent was removed under reduced pressure and the polymer was dissolved in petroleum ether and filtered through silica gel. The filtrate was concentrated and the remaining solvent was removed under vacuum to give a clear, colorless,  
20 viscous liquid. Yield = 0.2809 g.  $^1\text{H}$  NMR analysis: 136 Me/1000  $\text{CH}_2$ .

Example 487

A flame-dried 250 mL Schlenk flask was charged with 0.1384 g ( $1.007 \times 10^{-4}$  mol) of [(2-t-BuPh) $_2$ DABMe $_2$ ]PdMe(NCMe)BAF $^-$  in the glove box. The  
25 flask was twice evacuated and back-filled with ethylene and then cooled to  $-60^\circ\text{C}$ . The solid was dissolved in 100 mL of  $\text{CH}_2\text{Cl}_2$  and the flask was allowed to warm to room temperature with stirring under an atmosphere of ethylene. After stirring for 23 h the polymerization  
30 was quenched with methanol. The solvent was removed under reduced pressure and the polymer was dissolved in petroleum ether and filtered through silica gel. The filtrate was concentrated and the remaining solvent was removed under vacuum to give a clear, colorless,  
35 viscous liquid. Yield = 2.40 g.  $^1\text{H}$  NMR analysis: 123 Me/1000  $\text{CH}_2$ .

Example 488

Under inert conditions, a Schlenk tube was charged with 0.0142 g ( $1.02 \times 10^{-5}$  mol) of  $[(2-t-BuPh)_2DABAn]PdMe(Et_2O)BAF^-$ . The Schlenk tube was  
5 cooled to  $-78^\circ C$  and the solid was dissolved in 30 mL of  $CH_2Cl_2$ . A 300 mL autoclave was charged with 70 mL of  $CH_2Cl_2$  under an ethylene atmosphere. The cold catalyst solution was quickly transferred via cannula into the Parr® reactor and the reactor was pressurized to 172  
10 kPa (absolute). The polymerization was stirred for 20 h and the ethylene pressure was released. The red/orange solution was transferred and the solvent was removed under vacuum. A small amount of polyethylene remained after drying under vacuum overnight. Yield =  
15 0.17 g.  $^1H$  NMR analysis: 120 Me/1000  $CH_2$ .

Example 489

Following the procedure described in Example 488, 1.68 g of polyethylene was produced using 0.0140 g ( $1.02 \times 10^{-5}$  mol) of  $[(2-t-BuPh)_2DABMe_2]PdMe(NCMe)BAF^-$ .  
20 Yield = 1.68 g.  $^1H$  NMR analysis: 114 Me/1000  $CH_2$ .

Example 490

Under nitrogen,  $Ni(COD)_2$  (0.017 g, 0.062 mmol) and (2,4,6-MePh) $_2$ DABAn (0.026 g, 0.062 mmol) were dissolved in 2.00 g of cyclopentene to give a purple solution.  
25 The solution was then exposed to air for several seconds. The resulting dark red-brown solution was then put back under nitrogen, and  $EtAlCl_2$  (1 M solution in toluene, 3.0 mL, 3.0 mmol) was added. A cranberry-red solution formed instantly. The reaction mixture  
30 was stirred at room temperature for 3 days, during which time polycyclopentene precipitated. The reaction was then quenched by the addition of methanol followed by several drops of concentrated HCl. The reaction mixture was filtered, and the product polymer washed  
35 with methanol and dried to afford 0.92 g of polycyclopentene as an off-white powder. Thermal gravimetric analysis of this sample showed a weight loss starting at  $141^\circ C$ : the sample lost 18% of its

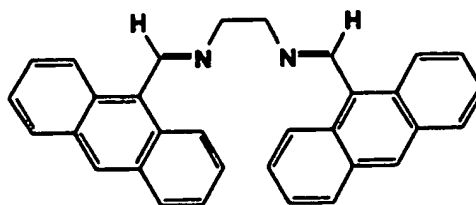
weight between 141 and 470°C, and the remaining material decomposed between 470 and 496°C.

Example 491

Under a nitrogen atmosphere, Ni(COD)<sub>2</sub> (0.017 g, 0.06 mmol) and MeC(=N-2,6-C<sub>6</sub>H<sub>3</sub>-iPr<sub>2</sub>)CH=C(NH-C<sub>6</sub>H<sub>3</sub>-iPr<sub>2</sub>)Me (0.025 g, 0.06 mmol) were dissolved in benzene (5.0 mL). To the resulting solution was added HBAF·(Et<sub>2</sub>O)<sub>2</sub> (0.060 g, 0.06 mmol). The resulting solution was immediately frozen inside a 40 mL shaker tube glass insert. The glass insert was transferred to a shaker tube, and its contents allowed to thaw under an ethylene atmosphere. The reaction mixture was agitated under 6.9 MPa C<sub>2</sub>H<sub>4</sub> for 40 h at ambient temperature. The final reaction mixture contained polyethylene, which was washed with methanol and dried; yield of polymer = 1.37 g. Branching per 1000 CH<sub>2</sub>'s was determined by <sup>13</sup>C NMR (C<sub>6</sub>D<sub>3</sub>Cl<sub>3</sub>): Total methyls (10.2), Methyl (8.8), Ethyl (1.1), Propyl (0), Butyl (0), ≥Am and end of chains (3.2), ≥Bu and end of chains (.3)

Example 492

Under a nitrogen atmosphere, Ni(COD)<sub>2</sub> (0.017 g, 0.06 mmol) and the ligand shown below (0.025 g, 0.06 mmol) were dissolved in benzene (5.0 mL). To the resulting solution was added HBAF·(Et<sub>2</sub>O)<sub>2</sub> (0.060 g, 0.06 mmol). The resulting solution was immediately frozen inside a 40 mL shaker tube glass insert. The glass insert was transferred to a shaker tube, and its contents allowed to thaw under an ethylene atmosphere. The reaction mixture was agitated under 6.9 MPa C<sub>2</sub>H<sub>4</sub> for 18 h at ambient temperature. The final reaction mixture contained polyethylene, which was washed with methanol and dried; yield of polymer = 11.0 g.



## Example 493

$\{[(2,6\text{-}i\text{-PrPh})_2\text{DABMe}_2]\text{Pd}(\eta^1\text{-CHEtPh})\}\text{BAF}$

In a nitrogen-filled drybox, 25 mL of Et<sub>2</sub>O was  
 5 added to a flask containing  $[(2,6\text{-}i\text{-PrPh})_2\text{DABMe}_2]\text{PdMeCl}$   
 (402 mg, 0.716 mmol) and NaBAF (633 mg, 0.714 mmol) to  
 yield an orange solution. Styrene (110  $\mu\text{L}$ , 0.960 mmol,  
 1.35 equiv) was dissolved in ~10 mL of Et<sub>2</sub>O and the  
 resulting solution was added to the reaction mixture,  
 10 which was then stirred for 3 h. Next, the solution was  
 filtered and the solvent was removed in vacuo. The  
 resulting orange powder (0.93 g, 87%) was washed with  
 hexane and dried in vacuo. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 MHz,  
 rt)  $\delta$  7.76 (s, 8, BAF: H<sub>O</sub>), 7.59 (s, 4, BAF: H<sub>P</sub>), 7.46  
 15 - 7.17 (m, 9, H<sub>aryl</sub>), 6.29 (d, 1, J = 7.33, H<sub>aryl</sub>), 5.65  
 (d, 1, J = 6.59, H<sub>aryl</sub>), 3.33, 3.13, 2.37 and 1.93  
 (septet, 1 each, J = 6.97 - 6.72, CHMe<sub>2</sub>, C'HMe<sub>2</sub>,  
 C''HMe<sub>2</sub>, C'''HMe<sub>2</sub>), 3.17 (dd, 1, J = 11.36, 3.66,  
 CHEtPh), 2.22 and 2.17 (s, 3 each, N=C(Me)-C'(Me)=N),  
 20 1.52, 1.45, 1.26, 1.26, 1.19, 1.15, 0.94 and 0.73 (d, 3  
 each, J = 6.97 - 6.59, CHMeMe', C'HMeMe', C''HMeMe',  
 C'''HMeMe'), 0.88 (t, 3, J = 0.88, CH(CH<sub>2</sub>CH<sub>3</sub>)Ph), 1.13  
 and -0.06 (m, 1 each, CH(CHH'CH<sub>3</sub>)Ph); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>,  
 75 MHz, rt)  $\delta$  176.6 and 174.0 (N=C-C'=N), 162.2 (q, J<sub>CB</sub>  
 25 = 49.3, BAF: C<sub>ipso</sub>), 142.8 and 142.4 (Ar, Ar': C<sub>ipso</sub>),  
 138.2, 137.3, 137.1, and 136.9 (Ar, Ar': C<sub>O</sub>), 135.2  
 (BAF: C<sub>O</sub>, C<sub>O'</sub>), 134.6 and 132.2 (Ph: C<sub>O</sub>, C<sub>m</sub>, or C<sub>p</sub>),  
 129.4 (BAF: C<sub>m</sub>), 129.0 and 128.5 (Ar, Ar': C<sub>p</sub>), 125.1,  
 125.1, 124.9 and 124.7 (Ar, Ar': C<sub>m</sub>), 125.1 (q, J<sub>CF</sub> =  
 30 272.5, BAF: CF<sub>3</sub>), 120.2 (Ph: C<sub>ipso</sub>) and 120.0 (Ph: C<sub>O</sub>,  
 C<sub>m</sub>, or C<sub>p</sub>), 117.9 (BAF: C<sub>p</sub>), 103.0 and 88.6 (Ph: C<sub>O'</sub>  
 and C<sub>m'</sub>), 69.1 (CHEtPh), 29.9, 29.7, 29.12 and 29.09  
 (CHMe<sub>2</sub>, C'HMe<sub>2</sub>, C''HMe<sub>2</sub>, C'''HMe<sub>2</sub>), 24.4, 24.3, 23.5,  
 23.4, 23.1, 23.0, 22.9, and 22.7 (CHMeMe', C'HMeMe',  
 35 C''HMeMe', C'''HMeMe'), 20.8, 20.65, and 20.61  
 (N=C(Me)-C'(Me)=N, CH(CH<sub>2</sub>CH<sub>3</sub>)Ph), 13.1 (CH(CH<sub>2</sub>CH<sub>3</sub>)Ph).

## Example 494

$\{[(2,6\text{-}i\text{-PrPh})_2\text{DABH}_2]\text{Pd}(\eta^3\text{-CHEt(4-C}_6\text{H}_4\text{-t-Bu)})\}\text{BAF}$   
 t-Butylstyrene (230  $\mu\text{L}$ , 1.26 mmol, 1.10 equiv) was  
 added via microliter syringe to a mixture of  $[(2,6\text{-}i\text{-}$   
 5  $\text{PrPh})_2\text{DABH}_2]\text{PdMeCl}$  (611 mg, 1.15 mmol) and NaBAF (1.01  
 g, 1.14 mmol) dissolved in 25 mL of  $\text{Et}_2\text{O}$ . An  
 additional 25 mL of  $\text{Et}_2\text{O}$  was added to the reaction  
 mixture, which was then stirred for ~12 h. The  
 resulting deep red solution was filtered, and the  
 10 solvent was removed in vacuo to yield a sticky red  
 solid. The solid was washed with 150 mL of hexane and  
 the product was dried in vacuo. A dull orange powder  
 (1.59 g, 91.7%) was obtained:  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ , 400 MHz,  
 rt)  $\delta$  8.34 and 8.16 (s, 1 each,  $\text{N}=\text{C}(\text{H})-\text{C}'(\text{H})=\text{N}$ ), 7.72  
 15 (s, 8, BAF:  $\text{H}_\text{O}$ ), 7.56 (s, 4, BAF:  $\text{H}_\text{P}$ ), 7.5 - 7.1 (m, 8,  
 $\text{H}_\text{Aryl}$ ), 6.88 (dd, 1,  $J = 7.1, 1.9$ ,  $\text{H}_\text{Aryl}$ ), 6.11 (dd, 1,  
 $J = 7.3, 2.0$ ,  $\text{H}_\text{Aryl}$ ), 3.49, 3.37, 2.64 and 2.44 (septet,  
 1 each,  $J = 6.6 - 6.9$ ,  $\text{CHMe}_2$ ,  $\text{C}'\text{HMe}_2$ ,  $\text{C}''\text{HMe}_2$  and  
 $\text{C}''' \text{HMe}_2$ ), 3.24 (dd, 1,  $J = 11.3, 4.1$ ,  $\text{CHEt(4-C}_6\text{H}_4\text{-t-}$   
 20  $\text{Bu})$ ), 1.52, 1.48, 1.24, 1.24, 1.19, 1.18, 1.0 and 0.70  
 (d, 3 each,  $J = 6.8 - 6.9$ ,  $\text{CHMeMe}'$ ,  $\text{C}'\text{HMeMe}'$ ,  
 $\text{C}''\text{HMeMe}'$ , and  $\text{C}''' \text{HMeMe}'$ ), 1.42 and 0.25 (m, 1 each,  
 $\text{CH}(\text{CHH}'\text{CH}_3)(4\text{-C}_6\text{H}_4\text{-t-Bu})$ ), 0.98 (s, 9, t-Bu), 0.87 (t,  
 3,  $J = 7.4$ ,  $\text{CH}(\text{CH}_2\text{CH}_3)(4\text{-C}_6\text{H}_4\text{-t-Bu})$ ;  $^{13}\text{C NMR}$  ( $\text{CD}_2\text{Cl}_2$ ,  
 25 100 MHz, rt)  $\delta$  165.0 ( $J_{\text{CH}} = 165$ ,  $\text{N}=\text{C}(\text{H})$ ), 163.3 ( $J_{\text{CH}} =$   
 165,  $\text{N}=\text{C}'(\text{H})$ ), 162.2 (q,  $J_{\text{CB}} = 49.9$ , BAF:  $\text{C}_{\text{ipso}}$ ), 157.0  
 ( $\text{C}_6\text{H}_4\text{-t-Bu: C}_\text{P}$ ), 144.9 and 144.6 (Ar, Ar':  $\text{C}_{\text{ipso}}$ ),  
 139.0, 138.4, 138.2 and 137.4 (Ar, Ar':  $\text{C}_\text{O}$ ,  $\text{C}_\text{O}'$ ), 135.2  
 (BAF:  $\text{C}_\text{O}$ ), 133.3, 129.8, 129.6 and 129.2 (Ar, Ar':  $\text{C}_\text{P}$ ;  
 30  $\text{C}_6\text{H}_4\text{-t-Bu: C}_\text{O}$ ,  $\text{C}_\text{m}$ ), 129.3 (q, BAF:  $\text{C}_\text{m}$ ), 125.0 (q,  $J_{\text{CF}} =$   
 272, BAF:  $\text{CF}_3$ ), 124.7, 124.64, 124.55, and 124.3 (Ar,  
 Ar':  $\text{C}_\text{m}$ ,  $\text{C}_\text{m}'$ ), 117.9 (BAF:  $\text{C}_\text{P}$ ), 119.1, 116.4 and 94.9  
 ( $\text{C}_6\text{H}_4\text{-t-Bu: C}_\text{m}'$ ,  $\text{C}_{\text{ipso}}$ ,  $\text{C}_\text{O}'$ ), 68.5 ( $\text{CHEt}$ ), 36.2 ( $\text{CMe}_3$ ),  
 30.2 ( $\text{CMe}_3$ ), 30.1, 29.9, 28.80 and 28.77 ( $\text{CHMe}_2$ ,  
 35  $\text{C}'\text{HMe}_2$ ,  $\text{C}''\text{HMe}_2$  and  $\text{C}''' \text{HMe}_2$ ), 25.0, 24.8, 24.1, 22.8,  
 22.7, 22.45, 22.36, and 22.1 ( $\text{CHMeMe}'$ ,  $\text{C}'\text{HMeMe}'$ ,  
 $\text{C}''\text{HMeMe}'$  and  $\text{C}''' \text{HMeMe}'$ ), 21.7 ( $\text{CH}(\text{CH}_2\text{CH}_3)$ ), 13.2  
 ( $\text{CH}(\text{CH}_2\text{CH}_3)$ ). Anal. Calcd for  $(\text{C}_{71}\text{H}_{67}\text{BF}_2\text{N}_2\text{Pd})$ : C,

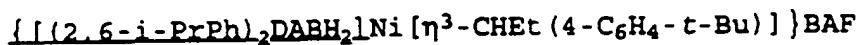
56.05; H, 4.44; N, 1.84. Found: C, 56.24; H, 4.22; N, 1.59.

#### Example 495



- 5 A solution of  $H_2C=CHC_6F_5$  (138 mg, 0.712 mmol) in 10 mL of  $Et_2O$  was added to a mixture of  $[(2.6-i-PrPh)_2DABMe_2]PdMeCl$  (401 mg, 0.713 mmol) and NaBAF (635 mg, 0.716 mmol) dissolved in 25 mL of  $Et_2O$ . After being stirred for 2 h, the reaction mixture was
- 10 filtered and the solvent was removed in vacuo. An orange powder (937 mg, 83.0%) was obtained.

#### Example 496



- In the drybox,  $\{[(2.6-i-PrPh)_2DABMe_2]NiMe(OEt_2)\}BAF$
- 15 (22.4 mg, 0.0161 mmol) was placed in an NMR tube. The tube was sealed with a septum and Parafilm®, removed from the drybox, and cooled to  $-78^\circ C$ .  $CD_2Cl_2$  (700  $\mu L$ ) and  $H_2C=CH(4-C_6H_4-t-Bu)$  (15  $\mu L$ , 5.10 equiv) were then added via gastight microliter syringe to the cold tube
- 20 in sequential additions. The septum was sealed with a small amount of grease and more Parafilm, the tube was shaken briefly and then transferred to the cold ( $-78^\circ C$ ) NMR probe. Insertion of *t*-butylstyrene was observed at  $-78^\circ C$  and was complete upon warming to  $-50^\circ C$  to yield
- 25 the  $\pi$ -benzyl complex:  $^1H$  NMR ( $CD_2Cl_2$ , 400 MHz,  $-50^\circ C$ ).  $\delta$  8.43 and 8.18 (s, 1 each,  $N=C(H)-C'(H)=N$ ), 7.76 (s, 8, BAF:  $H_O$ ), 7.58 (s, 4, BAF:  $H_P$ ), 7.5 - 7.1 (m, 8,  $H_{aryl}$ ), 6.80 (d, 1,  $J = 7.3$ ,  $H_{aryl}$ ), 6.15 (d, 1,  $J = 7.7$ ,  $H_{aryl}$ ), 3.72, 3.18, 2.68 and 2.50 (septet, 1 each,  $J =$
- 30 6.5 - 6.7,  $CHMe_2$ ,  $C'HMe_2$ ,  $C''HMe_2$  and  $C'''HMe_2$ ), 2.56 (dd, 1,  $J = 11.5$ , 3.9,  $CH_2$ ), 1.6 - 0.8 ( $CHMeMe'$ ,  $C'HMeMe'$ ,  $C''HMeMe'$ ,  $C'''HMeMe'$ , and  $CH(CHH'CH_3)$ ), 0.94 (s, 9,  $CMe_3$ ), 0.72 (t, 3,  $J = 7.3$ ,  $CH(CH_2CH_3)$ ), -0.04 (m, 1,  $CH(CHH'CH_3)$ ).

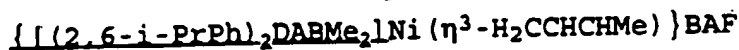


Examples 497-515General Procedure for the Synthesis of  $\pi$ -Allyl Type  
Nickel Compounds

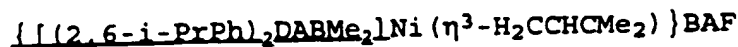
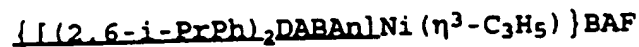
A mixture of one equiv. of the appropriate  $\alpha$ -  
5 diimine, one equiv of NaBAF, and 0.5 equiv of  
[(allyl)Ni( $\mu$ -X)]<sub>2</sub> (X = Cl or Br) was dissolved in Et<sub>2</sub>O.  
The reaction mixture was stirred for ~2 h before being  
filtered. The solvent was removed in vacuo to yield  
the desired product, generally as a red or purple  
10 powder. (The [(allyl)Ni( $\mu$ -X)]<sub>2</sub> precursors were  
synthesized according to the procedures published in  
the following reference: Wilke, G.; Bogdanovic, B.;  
Hardt, P.; Heimbach, P.; Keim, W.; Kroner, M.;  
Oberkirch, W.; Tanaka, K.; Steinrucke, E.; Walter, D.;  
15 Zimmermann, H. Angew. Chem. Int. Ed. Engl. 1966, 5,  
151-164.) The following compounds were synthesized  
according to the above general procedure.

Example 497

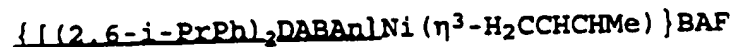
20

Example 498Example 499Example 500

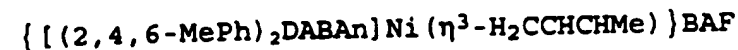
25

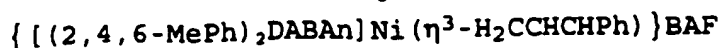
Example 501Example 502

30

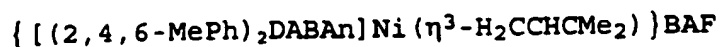
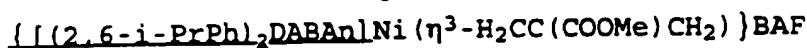
Example 503Example 504Example 505

35

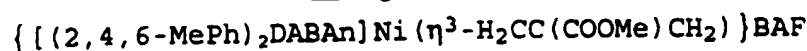
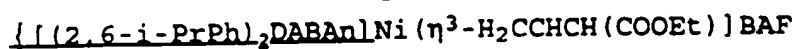
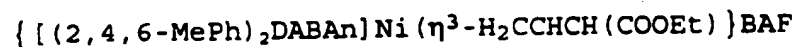
Example 506

Example 507Example 508

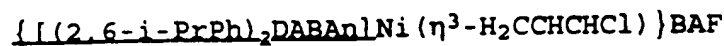
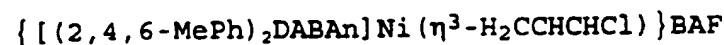
5

Example 509Example 510Example 511

10

Example 512Example 513

15

Example 514Example 515Examples 516-537

20

Polymerizations catalyzed by nickel and palladium  $\pi$ -benzyl initiators and by nickel allyl initiators are illustrated in the following Table containing Examples 516-537. The initiation of polymerizations catalyzed by nickel allyl initiators where the allyl ligand was substituted with functional groups, such as chloro or ester groups, was often aided by the addition of a Lewis acid.

25

Example	Compound	Conditions	Results
516	$\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{Pd}(\eta^3\text{-CHEtPh})\}\text{BAF}$	0.067 mmol Cmpd; 25 °C; 1 atm E; 2 days; $\text{CH}_2\text{Cl}_2$	<0.5 g PE (270 TO)
517	$\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{Pd}(\eta^3\text{-CHEtPh})\}\text{BAF}$	0.027 mmol Cmpd; 25 °C; 6.9 MPa E; 18 h; $\text{C}_6\text{D}_6$	8.2 g PE (11,000 TO)
518	$\{[(2,6\text{-i-PrPh})_2\text{DABH}_2]\text{Pd}(\eta^3\text{-CHEt(4-C}_6\text{H}_4\text{-i-Bu)})\}\text{BAF}$	0.016 mmol Cmpd; 25 °C; 6.9 MPa E; 18 h; $\text{C}_6\text{D}_6$	1.5 g PE (3,300 TO)
519	$\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{Pd}(\eta^3\text{-CHEtC}_6\text{F}_5)\}\text{BAF}$	0.063 mmol Cmpd; 25 °C; 1 atm E; 5 days; $\text{CH}_2\text{Cl}_2$	4.6 g PE (2,600 TO)
520	$\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{Pd}(\eta^3\text{-CHEtC}_6\text{F}_5)\}\text{BAF}$	0.044 mmol Cmpd; 25 °C; 6.9 MPa E; 18 h; $\text{C}_6\text{D}_6$	6.4 g PE (5,200 TO)
521	$\{[(2,4,6\text{-MePh})_2\text{DABAn}]\text{Ni}(\eta^3\text{-H}_2\text{CCHCMe}_2)\}\text{BAF}$	0.049 mmol Cmpd; 25 °C; 6.9 MPa E; 18 h; $\text{C}_6\text{D}_6$	1.5 g PE (1,100 TO)
522	$\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{Ni}(\eta^3\text{-H}_2\text{CCHCMe}_2)\}\text{BAF}$	0.034 mmol Cmpd; 25 °C; 6.9 MPa E; 18 h; $\text{C}_6\text{D}_6$	35 mg PE (37 TO)
523	$\{[(2,4,6\text{-MePh})_2\text{DABMe}_2]\text{Ni}(\eta^3\text{-C}_3\text{H}_5)\}\text{BAF}$	0.047 mmol Cmpd; 80 °C; 6.9 MPa E; 18 h; $\text{C}_6\text{D}_6$	20 mg PE (15 TO)
524	$\{[(2,4,6\text{-MePh})_2\text{DABAn}]\text{Ni}(\eta^3\text{-C}_3\text{H}_5)\}\text{BAF}$	0.034 mmol Cmpd; 80 °C; 6.9 MPa E; 18 h; $\text{C}_6\text{D}_6$	260 mg PE (270 TO)
525	$\{[(2,4,6\text{-MePh})_2\text{DABAn}]\text{Ni}(\eta^3\text{-H}_2\text{CCHCHPh})\}\text{BAF}$	0.026 mmol Cmpd; 80 °C; 6.9 MPa E; 18 h; $\text{C}_6\text{D}_6$	141 mg PE (190 TO)
526	$\{[(2,6\text{-i-PrPh})_2\text{DABAn}]\text{Ni}(\eta^3\text{-H}_2\text{CCHCHPh})\}\text{BAF}$	0.040 mmol Cmpd; 80 °C; 6.9 MPa E; 18 h; $\text{C}_6\text{D}_6$	992 mg PE (880 TO)

527	$\{[(2,6\text{-i-PrPh})_2\text{DABAn}]\text{Ni}(\eta^3\text{-H}_2\text{CCHCHMe})\}\text{BAF}$	0.043 mmol Compd; 80 °C; 6.9 MPa E; 18 h; C <sub>6</sub> D <sub>6</sub>	23 mg PE (19 TO)
528	$\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{Ni}(\eta^3\text{-H}_2\text{CCHCHMe}_2)\}\text{BAF}$	0.044 mmol Compd; 80 °C; 6.9 MPa E; 18 h; C <sub>6</sub> D <sub>6</sub>	54 mg PE (44 TO)
529	$\{[(2,6\text{-i-PrPh})_2\text{DABAn}]\text{Ni}(\eta^3\text{-C}_3\text{H}_5)\}\text{BAF}$	0.042 mmol Compd; 80 °C; 6.9 MPa E; 18 h; C <sub>6</sub> D <sub>6</sub>	15 mg PE (13 TO)
530	$\{[(2,4,6\text{-MePh})_2\text{DABAn}]\text{Ni}(\eta^3\text{-H}_2\text{CCHCHCl})\}\text{BAF}$	0.043 mmol Compd; 25 °C; 6.9 MPa E; 18 h; C <sub>6</sub> D <sub>6</sub>	94 mg PE (78 TO)
531	$\{[(2,6\text{-i-PrPh})_2\text{DABAn}]\text{Ni}(\eta^3\text{-H}_2\text{CCHCHCl})\}\text{BAF}$	0.042 mmol Compd; 25 °C; 6.9 MPa E; 18 h; C <sub>6</sub> D <sub>6</sub>	8 mg PE (7 TO)
532	$\{[(2,4,6\text{-MePh})_2\text{DABAn}]\text{Ni}(\eta^3\text{-H}_2\text{CCHCHCl})\}\text{BAF}$	0.020 mmol Compd; 0.04 mmol B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> ; 25 °C; 6.9 MPa E; 18 h; CDCl <sub>3</sub>	7.8 g PE (14,000 TO)
533	$\{[(2,4,6\text{-MePh})_2\text{DABAn}]\text{Ni}(\eta^3\text{-H}_2\text{CCHCHCl})\}\text{BAF}$	0.020 mmol Compd; 0.04 mmol BPh <sub>3</sub> ; 25 °C; 6.9 MPa E; 18 h; CDCl <sub>3</sub>	8.4 g PE (15,000 TO)
534	$\{[(2,6\text{-i-PrPh})_2\text{DABAn}]\text{Ni}(\eta^3\text{-H}_2\text{CCHCH}(\text{COOEt}))\}\text{BAF}$	0.020 mmol Compd; 0.04 mmol BPh <sub>3</sub> ; 25 °C; 6.9 MPa E; 18 h; CDCl <sub>3</sub>	4.7 g PE (8,400 TO)
535	$\{[(2,6\text{-i-PrPh})_2\text{DABAn}]\text{Ni}(\eta^3\text{-H}_2\text{CCHCHCl})\}\text{BAF}$	0.020 mmol Compd; 0.04 mmol BPh <sub>3</sub> ; 80 °C; 6.9 MPa E; 18 h; C <sub>6</sub> D <sub>6</sub>	6.8 g PE (12,000 TO)
536	$\{[(2,6\text{-i-PrPh})_2\text{DABAn}]\text{Ni}(\eta^3\text{-H}_2\text{CCHCHCl})\}\text{BAF}$	0.020 mmol Compd; 10 mg montmorillonite; 80 °C; 6.9 MPa E; 18 h; C <sub>6</sub> D <sub>6</sub>	326 mg PE (580 TO)

537	$\{[(2,6\text{-}i\text{-PrPh})_2\text{DABAn}]\text{Ni}(\eta^3\text{-H}_2\text{CCHCH}(\text{COOEt}))\}\text{BAF}$	0.020 mmol Compd; 0.04 mmol BPh <sub>3</sub> ; 80 °C; 6.9 MPa E; 18 h; C <sub>6</sub> D <sub>6</sub>	10.3 g PE (18,000 TO)
-----	--	--	-----------------------

What is claimed is:

1. A polyolefin, which contains about 80 to about 150 branches per 1000 methylene groups, and which contains for every 100 branches that are methyl, about  
5 30 to about 90 ethyl branches, about 4 to about 20 propyl branches, about 15 to about 50 butyl branches, about 3 to about 15 amyl branches, and about 30 to about 140 hexyl or longer branches.

2. The polyolefin as recited in claim 1 which  
10 contains about 100 to about 130 branches per 1000 methylene groups, and which contains for every 100 branches that are methyl, about 50 to about 75 ethyl branches, about 5 to about 15 propyl branches, about 24 to about 40 butyl branches, about 5 to about 10 amyl  
15 branches, and about 65 to about 120 hexyl or longer branches.

3. The polyolefin as recited in claim 1 which is an ethylene homopolymer.

4. A polyolefin which contains about 20 to about  
20 150 branches per 1000 methylene groups, and which contains for every 100 branches that are methyl, about 4 to about 20 ethyl branches, about 1 to about 12 propyl branches, about 1 to about 12 butyl branches, about 1 to about 10 amyl branches, and 0 to about 20  
25 hexyl or longer branches.

5. The polyolefin as recited in claim 4 which contains about 40 to about 100 branches per 1000 methylene groups, and which contains for every 100 branches that are methyl, about 6 to about 15 ethyl  
30 branches, about 2 to about 10 propyl branches, about 2 to about 10 butyl branches, about 2 to about 8 amyl branches, and about 2 to about 15 hexyl or longer branches.

6. The polyolefin as recited in claim 4 which is  
35 an ethylene homopolymer.

7. A polymer, consisting essentially of units derived from the monomers ethylene and a compound of the formula  $\text{CH}_2=\text{CH}(\text{CH}_2)_m\text{CO}_2\text{R}^1$ , wherein  $\text{R}^1$  is hydrogen,

hydrocarbyl or substituted hydrocarbyl, and m is 0 or an integer from 1 to 16, and which contains about 0.01 to about 40 mole percent of repeat units derived from said compound, and provided that said repeat units  
 5 derived from said compound are in branches of the formula  $-\text{CH}(\text{CH}_2)_n\text{CO}_2\text{R}^1$ , in about 30 to about 70 mole percent of said branches n is 5 or more, in about 0 to about 20 mole percent n is 4, in about 3 to 60 mole percent n is 1, 2 and 3, and in about 1 to about 60  
 10 mole percent n is 0.

8. The polymer as recited in claim 7 wherein m is 0.

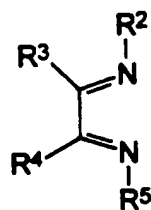
9. The polymer as recited in claim 7 wherein  $\text{R}^1$  is hydrocarbyl or substituted hydrocarbyl.

15 10. The polymer as recited in claim 7 wherein  $\text{R}^1$  is alkyl containing 1 to 10 carbon atoms.

11. The polymer as recited in claim 8 wherein  $\text{R}^1$  is hydrocarbyl or substituted hydrocarbyl.

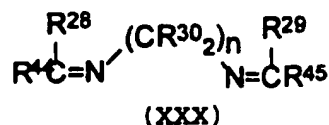
12. The polymer as recited in claim 7 wherein  
 20 about 0.1 to about 20 mole percent of said units are derived from said compound.

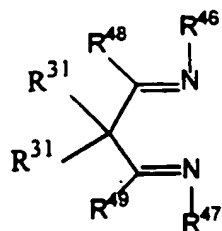
13. A process for the polymerization of olefins, comprising, contacting a transition metal complex of a bidentate ligand selected from the group consisting of



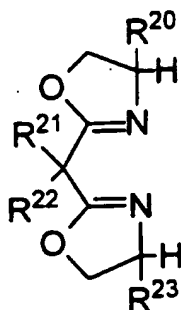
25

(VIII)





(XXIII)



(XXXII)

5 with an olefin wherein:

said olefin is selected from the group consisting of ethylene, an olefin of the formula  $R^{17}CH=CH_2$  or  $R^{17}CH=CHR^{17}$ , cyclobutene, cyclopentene, norbornene, or a substituted norbornene,;

10 said transition metal is selected from the group consisting of Ti, Zr, Sc, V, Cr, a rare earth metal, Fe, Co, Ni or Pd;

$R^2$  and  $R^5$  are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom  
15 bound to the imino nitrogen atom has at least two carbon atoms bound to it;

$R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or  $R^3$  and  $R^4$  taken together are hydrocarbylene or substituted  
20 hydrocarbylene to form a carbocyclic ring;

$R^{44}$  is hydrocarbyl or substituted hydrocarbyl, and  $R^{28}$  is hydrogen, hydrocarbyl or substituted hydrocarbyl or  $R^{44}$  and  $R^{28}$  taken together form a ring;



$R^{45}$  is hydrocarbyl or substituted hydrocarbyl,  
and  $R^{29}$  is hydrogen, substituted hydrocarbyl or  
hydrocarbyl, or  $R^{45}$  and  $R^{29}$  taken together form a ring;

each  $R^{30}$  is independently hydrogen, substituted  
5 hydrocarbyl or hydrocarbyl, or two of  $R^{30}$  taken  
together form a ring;

$R^{20}$  and  $R^{23}$  are independently hydrocarbyl or  
substituted hydrocarbyl;

$R^{21}$  and  $R^{22}$  are each independently hydrogen,  
10 hydrocarbyl or substituted hydrocarbyl;

each  $R^{17}$  is independently hydrocarbyl or  
substituted hydrocarbyl provided that any olefinic bond  
in said olefin is separated from any other olefinic  
bond or aromatic ring by a quaternary carbon atom or at  
15 least two saturated carbon atoms;

$R^1$  is hydrogen, hydrocarbyl or substituted  
hydrocarbyl;

$n$  is 2 or 3;

and provided that:

20 when said bidentate ligand is (XXX) M is not  
Pd;

when M is Pd a diene is not present; and  
said transition metal also has bonded to it a  
ligand that may be displaced by said olefin or add to  
25 said olefin;

when norbornene or substituted norbornene is  
used no other olefin is present.

14. The process as recited in claim 13 wherein  
said transition metal is Co, Fe, Ni or Pd.

30 15. The process as recited in claim 13 wherein  
said transition metal is Ni or Pd.

16. The process as recited in claim 13 or 15  
wherein said olefin is ethylene,  $R^{17}CH=CH_2$ , or  
cyclopentene, wherein  $R^{17}$  is n-alkyl.

35 17. The process as recited in claim 13 wherein  
said olefin comprises cyclopentene.

18. The process as recited in claim 13, 14, 15, or  
16 wherein said bidentate ligand is (VIII).

19. The process as recited in claim 18 wherein said olefin is ethylene.

20. The process as recited is in claim 18 wherein said olefin is propylene.

5 21. The process as recited in claim 18 wherein said olefin is a combination of ethylene and propylene.

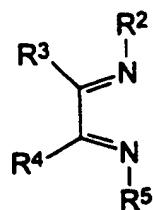
22. The process as recited in claim 18 wherein said olefin is contained in a mixed butenes stream.

10 23. The process as recited in claim 18 wherein  $R^2$  and  $R^5$  are each independently hydrocarbyl provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;  $R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, or  $R^3$  and  $R^4$  taken together are hydrocarbylene to form a carbocyclic ring.

15 24. The process as recited in claim 18 wherein  $R^3$  and  $R^4$  are each independently hydrogen or methyl or together are 1,8-naphthylidene, and both  $R^2$  and  $R^5$  are 2,6-diisopropylphenyl.

20 25. The process as recited in claim 18 wherein said olefin comprises cyclopentene.

26. A process for the copolymerization of an olefin and a fluorinated olefin, comprising, contacting a transition metal complex of a bidentate ligand selected from the group consisting of



25

(VIII) "

with an olefin, and a fluorinated olefin wherein:

30 said olefin is selected from the group consisting of ethylene and an olefin of the formula  $R^{17}CH=CH_2$  or  $R^{17}CH=CHR^{17}$ ;

said transition metal is selected from the group consisting of Ni and Pd;

said fluorinated olefin is of the formula  
 $H_2C=CH(CH_2)_aR_fR^{42}$ ;

a is an integer of 2 to 20;  $R_f$  is  
perfluoroalkylene optionally containing one or more  
5 ether groups;

$R^{42}$  is fluorine or a functional group;

$R^2$  and  $R^5$  are each independently hydrocarbyl or  
substituted hydrocarbyl, provided that the carbon atom  
bound to the imino nitrogen atom has at least two  
10 carbon atoms bound to it;

$R^3$  and  $R^4$  are each independently hydrogen,  
hydrocarbyl, substituted hydrocarbyl, or  $R^3$  and  $R^4$   
taken together are hydrocarbylene or substituted  
hydrocarbylene to form a carbocyclic ring;

15 each  $R^{17}$  is independently saturated  
hydrocarbyl;

and provided that said transition metal also has  
bonded to it a ligand that may be displaced by said  
olefin or added to said olefin.

20 27. The process as recited in claim 26 wherein  $R^{42}$   
is fluorine, ester or sulfonyl halide.

28. The process as recited in claim 26 wherein  $R_f$   
is  $-(CF_2)_b-$ , wherein b is 2 to 20, or  $-(CF_2)_dOCF_2CF_2-$   
wherein d is 2 to 20.

25 29. The process as recited in claim 26 or 27  
wherein said olefin is ethylene or wherein said olefin  
is  $R^{17}CH=CH_2$ , wherein  $R^{17}$  is n-alkyl.

30 30. The process as recited in claim 26 wherein  $R^2$   
and  $R^5$  are each independently hydrocarbyl, provided  
that the carbon atom bound to the imino nitrogen atom  
has at least two carbon atoms bound to it; and  $R^3$  and  
 $R^4$  are each independently hydrogen, hydrocarbyl, or  $R^3$   
and  $R^4$  taken together are hydrocarbylene to form a  
carbocyclic ring.

35 31. A copolymer of an olefin of the formula  
 $R^{17}CH=CHR^{17}$  and a fluorinated olefin of the formula  
 $H_2C=CH(CH_2)_aR_fR^{42}$ , wherein:

each  $R^{17}$  is independently hydrogen or saturated hydrocarbyl;

a is an integer of 2 to 20;  $R_f$  is perfluoroalkylene optionally containing one or more  
5 ether groups; and

$R^{42}$  is fluorine or a functional group;  
provided that when both of  $R^{17}$  are hydrogen and  $R^{42}$   
is fluorine,  $R_f$  is  $-(CF_2)_b-$  wherein b is 2 to 20 or  
perfluoroalkylene containing at least one ether group.

10 32. The copolymer as recited in claim 31 wherein  
 $R^{42}$  is fluorine, ester, sulfonic acid, or sulfonyl  
halide.

33. The copolymer as recited in claim 31 wherein  
 $R_f$  is  $-(CF_2)_b-$ , wherein b is 2 to 20, or  $-(CF_2)_dOCF_2CF_2-$   
15 wherein d is 2 to 20.

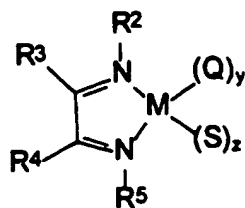
34. The copolymer as recited in claim 31 or 32  
wherein said olefin is ethylene or wherein said olefin  
is  $R^{17}CH=CH_2$ , wherein  $R^{17}$  is n-alkyl.

35. The copolymer as recited in claim 31 wherein  
20 said fluorinated olefin is about 1 to 20 mole percent  
of repeat units in said copolymer.

36. An acid catalyst of the composition of claim  
31, wherein  $R^{42}$  is sulfonic acid.

37. A process for the polymerization of olefins,  
25 comprising, contacting, at a temperature of about  
-100°C to about +200°C:

a first compound W, which is a neutral Lewis  
acid capable of abstracting either  $Q^-$  or  $S^-$  to form  $WQ^-$   
or  $WS^-$ , provided that the anion formed is a weakly  
30 coordinating anion; or a cationic Lewis or Bronsted  
acid whose counterion is a weakly coordinating anion;  
a second compound of the formula



(XI)

and one or more monomers selected from the group consisting of ethylene, an olefin of the formula  
 5  $R^{17}CH=CH_2$ , or  $R^{17}CH=CHR^{17}$ , cyclobutene, cyclopentene, substituted norbornene, or norbornene;

wherein:

M is Ti, Zr, Sc, V, Cr, a rare earth metal, Fe, Co, Ni or Pd in the m oxidation state;

10  $y + z = m$

$R^2$  and  $R^5$  are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

15  $R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or  $R^3$  and  $R^4$  taken together are hydrocarbylene or substituted hydrocarbylene to form a carbocyclic ring;

20 each  $R^{17}$  is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

25 Q is alkyl, hydride, chloride, iodide, or bromide;

S is alkyl, hydride, chloride, iodide, or bromide; and

provided that;

30 when norbornene or substituted norbornene is present, no other monomer is present;

when M is Pd a diene is not present; and

except when M is Pd, when both Q and S are each independently chloride, bromide or iodide W is capable of transferring a hydride or alkyl group to M.

38. The process as recited in claim 37 wherein  
5 said monomer is ethylene only.

39. The process as recited in claim 37 wherein  
said monomer is an  $\alpha$ -olefin only.

40. The process as recited in claim 39 wherein  
said  $\alpha$ -olefin is propylene.

10 41. The process as recited in claim 37 done in the  
presence of a solvent.

42. The process as recited in claim 41 wherein  $R^3$   
and  $R^4$  are each independently hydrogen or methyl, or  $R^3$   
and  $R^4$  taken together are 1,8-naphthylylene, and both  
15  $R^2$  and  $R^5$  are 2,6-diisopropylphenyl.

43. The process as recited in claim 37 used to  
make a block polymer.

44. The process as recited in claim 37 wherein:  
M is Ti(IV), Q and S are chloride, and y and z are  
20 2;

M is Zr(IV), Q and S are chloride, and y and z are  
2;

M is Co(II), Q and S are bromide, and y and z are  
1;

25 M is Fe(II), Q and S are chloride, and y and z are  
1;

M is Sc(III), Q and S are chloride, y is 1 and z  
is 2;

30 M is Ni(II), Q and S are bromide or chloride, and  
y and z are 1;

M is Pd(II), Q and S are methyl, and y and z are  
1;

M is Pd(II), Q and S are chloride, and y and z are  
1;

35 M is Ni(I), Q is methyl, chloride, bromide, iodide  
or acetylacetonate, y is 1, and z is 0;

M is Pd(II), Q is methyl and S is chloride, and y  
and z are 1; or

M is Ni(II), Q and S are methyl, and y and z are 1.

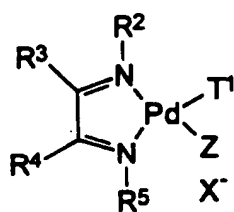
45. The process as recited in claim 37 wherein ethylene and propylene are the monomers.

5 46. The process as recited in claim 37 wherein said monomers are part of a crude butenes stream.

47. The process as recited in claim 37 wherein R<sup>2</sup> and R<sup>5</sup> are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; R<sup>3</sup> and R<sup>4</sup> are each independently hydrogen, hydrocarbyl, or R<sup>3</sup> and R<sup>4</sup> taken together are hydrocarbylene to form a carbocyclic ring.

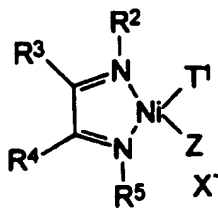
15 48. The process as recited in claim 37 wherein said monomer comprises cyclopentene.

49. A process for the production of polyolefins, comprising, contacting, at a temperature of about -100°C to about +200°C, one or more monomers selected from the group consisting of ethylene, an olefin of the formula R<sup>17</sup>CH=CH<sub>2</sub>, or R<sup>17</sup>CH=CHR<sup>17</sup>, cyclobutene, 20 cyclopentene, substituted norbornene, and norbornene; and a compound of the formula

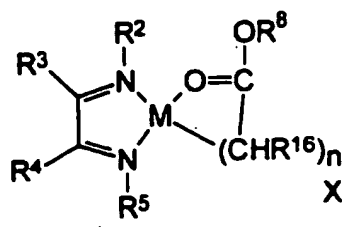


25

(II)

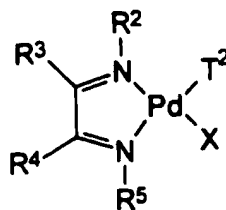


(III)



(IV)

or



(VII)

wherein:

5  $R^2$  and  $R^5$  are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

10  $R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or  $R^3$  and  $R^4$  taken together are hydrocarbylene or substituted hydrocarbylene to form a carbocyclic ring;

$T^1$  is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds,  $R^{15}C(=O)-$  or  $R^{15}OC(=O)-$ ;

15  $Z$  is a neutral Lewis base wherein the donating atom is nitrogen, sulfur or oxygen, provided that if the donating atom is nitrogen then the  $pK_a$  of the conjugate acid of that compound is less than about 6;

$X$  is a weakly coordinating anion;

20  $R^{15}$  is hydrocarbyl not containing olefinic or acetylenic bonds;

each  $R^{17}$  is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

$M$  is Ni(II) or Pd(II);

each  $R^{16}$  is independently hydrogen or alkyl containing 1 to 10 carbon atoms;

$n$  is 1, 2, or 3;

30  $R^8$  is hydrocarbyl; and

$T^2$  is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, hydrocarbyl substituted



with keto or ester groups but not containing olefinic or acetylenic bonds,  $R^{15}C(=O)-$  or  $R^{15}OC(=O)-$ ;

provided that:

when M is Pd, or (II) or (VII) are present, a  
5 diene is not present; and

when norbornene or substituted norbornene is used no other monomer is present.

50. The process as recited in claim 49 wherein said monomer is ethylene only.

10 51. The process as recited in claim 49 wherein said monomer is an  $\alpha$ -olefin only.

52. The process as recited in claim 51 wherein said  $\alpha$ -olefin is propylene.

53. The process as recited in claim 49 wherein  
15 said compound is (II), (IV) or (VII), M is Pd(II), and a comonomer selected from the group consisting of: a compound of the formula  $CH_2=CH(CH_2)_mCO_2R^1$ , wherein  $R^1$  is hydrogen or, hydrocarbyl or substituted hydrocarbyl containing 1 to 10 carbon atoms, and m is 0 or an  
20 integer of 1 to 16; CO; and a vinyl ketone, is also present.

54. The process as recited in claim 53 wherein m is 0, and  $R^1$  is hydrocarbyl or substituted hydrocarbyl.

55. The process as recited in claim 49 done in the  
25 presence of a solvent.

56. The process as recited in claim 49 done in the absence of a solvent.

57. The process as recited in claim 49 wherein  $R^3$  and  $R^4$  are each independently hydrogen or methyl, or  $R^3$   
30 and  $R^4$  taken together are 1,8-naphthylylene, and both  $R^2$  and  $R^5$  are 2,6-diisopropylphenyl.

58. The process as recited in claim 49 used to make a block polymer.

59. The process as recited in claim 49 wherein X  
35 is BAF,  $SbF_6$ ,  $PF_6$ , or  $BF_4$ .

60. The process as recited in claim 57 wherein X is BAF,  $SbF_6$ ,  $PF_6$ , or  $BF_4$ .

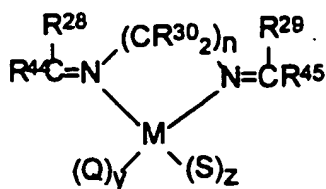
61. The process as recited in claim 60 wherein a monomer is ethylene or propylene.

62. The process as recited in claim 49 wherein the monomers are ethylene and propylene.

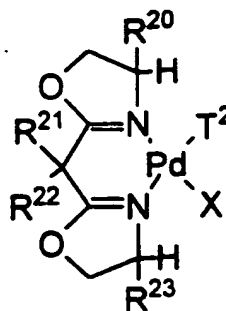
5        63. The process as recited in claim 49 wherein said monomers are part of a crude butenes stream.

64. The process as recited in claim 49 wherein  $R^2$  and  $R^5$  are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom  
10       has at least two carbon atoms bound to it;  $R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, or  $R^3$  and  $R^4$  taken together are hydrocarbylene to form a carbocyclic ring.

65. A process for the production of polyolefins,  
15       comprising contacting, at a temperature of about  $-100^{\circ}\text{C}$  to about  $+200^{\circ}\text{C}$ , one or more monomers selected from the group consisting of ethylene, an olefin of the formula  $R^{17}\text{CH}=\text{CH}_2$  or  $R^{17}\text{CH}=\text{CHR}^{17}$ , cyclobutene, cyclopentene, substituted norbornene, and norbornene; with a compound  
20       of the formula

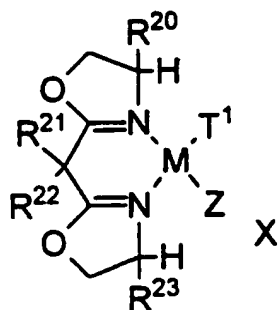


(XVII)



(XVIII)

or



(XIII)

wherein:

- 5  $R^{44}$  is hydrocarbyl or substituted hydrocarbyl,  
and  $R^{28}$  is hydrogen, hydrocarbyl or substituted  
hydrocarbyl or  $R^{44}$  and  $R^{28}$  taken together form a ring;  
 $R^{45}$  is hydrocarbyl or substituted hydrocarbyl,  
and  $R^{29}$  is hydrogen, substituted hydrocarbyl or  
10 hydrocarbyl, or  $R^{45}$  and  $R^{29}$  taken together form a ring;  
each  $R^{30}$  is independently hydrogen, substituted  
hydrocarbyl or hydrocarbyl or two of  $R^{30}$  taken together  
form a ring;  $R^{20}$  and  $R^{23}$  are independently hydrocarbyl or  
substituted hydrocarbyl;  
15  $R^{21}$  and  $R^{22}$  are each independently hydrogen,  
hydrocarbyl or substituted hydrocarbyl;  
 $n$  is 2 or 3;  
 $T^1$  is hydrogen, hydrocarbyl not containing  
olefinic or acetylenic bonds,  $R^{15}C(=O)-$  or  $R^{15}OC(=O)-$ ;  
20  $M$  is Ti, Zr, Sc, Cr, a rare earth metal, V, Fe,  
Co, Ni or Pd the  $m$  oxidation state;  
for (XVII),  $y + z = m$ ;

for (XIII), m is 2;

Q is alkyl, hydride, chloride, iodide, or  
bromide;

S is alkyl, hydride, chloride, iodide, or  
5 bromide;

T<sup>2</sup> is hydrogen, hydrocarbyl not containing  
olefinic or acetylenic bonds, hydrocarbyl substituted  
with keto or ester groups but not containing olefinic  
or acetylenic bonds, R<sup>15</sup>C(=O)- or R<sup>15</sup>OC(=O)-;

10 Z is a neutral Lewis base wherein the donating  
atom is nitrogen, sulfur or oxygen, provided that if  
the donating atom is nitrogen then the pKa of the  
conjugate acid of that compound is less than about 6;  
and

15 X is a weakly coordinating anion; and  
provided that:

when said compound is (XVII) M is not Pd; and

except when M is Pd, when both Q and S are each  
independently chloride, bromide or iodide W is capable  
20 of transferring a hydride or alkyl group to M.

66. The process as recited in claim 65 wherein  
said monomer is ethylene only.

67. The process as recited in claim 65 wherein  
said monomer is an  $\alpha$ -olefin only.

25 68. The process as recited in claim 67 wherein  
said  $\alpha$ -olefin is propylene.

69. The process as recited in claim 66 wherein M  
is Pd(II) and one or more comonomer is selected from  
the group consisting of: a compound of the formula  
30  $\text{CH}_2=\text{CH}(\text{CH}_2)_m\text{CO}_2\text{R}^1$ , wherein R<sup>1</sup> is hydrogen or, hydrocarbyl  
or substituted hydrocarbyl containing 1 to 10 carbon  
atoms, and m is 0 or an integer of 1 to 16; CO; and a  
vinyl ketone is also present.

70. The process as recited in claim 69 wherein m  
35 is 0, and R<sup>1</sup> is hydrocarbyl or substituted hydrocarbyl.

71. The process as recited in claim 65 done in the  
presence of a solvent.

PCL XL error

Subsystem: IMAGE

Error: MissingData

Operator: ReadImage

Position: 2624

230. The process as recited in claim 216 wherein:

$R^{46}$  and  $R^{47}$  are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

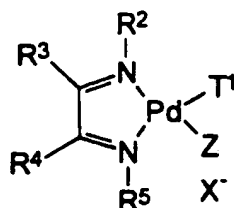
$R^{48}$  and  $R^{49}$  are each independently hydrogen, hydrocarbyl, or substituted hydrocarbyl;

each  $R^{31}$  is independently hydrocarbyl, substituted hydrocarbyl, or hydrogen; and

each  $R^{17}$  is hydrocarbyl.

231. The process as recited in claim 216 wherein said olefin comprises cyclopentene.

232. A compound of the formula



(II)

wherein:

$R^2$  and  $R^5$  are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

$R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or  $R^3$  and  $R^4$  taken together are hydrocarbylene or substituted hydrocarbylene to form a carbocyclic ring;

$T^1$  is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds,  $R^{15}C(=O)-$  or  $R^{15}OC(=O)-$ ;

$Z$  is a neutral Lewis base wherein the donating atom is nitrogen, sulfur or oxygen, provided that if the donating atom is nitrogen then the pKa of the conjugate acid of that compound is less than about 6;

$X$  is a weakly coordinating anion; and

$R^{15}$  is hydrocarbyl not containing olefinic or acetylenic bonds;

provided that when  $R^3$  and  $R^4$  taken together are hydrocarbylene to form a carbocyclic ring Z is not an organic nitrile.

233. The compound as recited in claim 232 wherein  $T^1$  is methyl, and Z is  $R^6_2O$  or  $R^7CN$  wherein each  $R^6$  independently hydrogen or hydrocarbyl and  $R^7$  is hydrocarbyl.

10 234. The compound as recited in claim 232 wherein  $R^3$  and  $R^4$  are each independently hydrogen or methyl or  $R^3$  and  $R^4$  taken together are 1,8-naphthylidene, and both  $R^2$  and  $R^5$  are 2,6-diisopropylphenyl.

235. The compound as recited in claim 233 wherein 15  $R^3$  and  $R^4$  are each independently hydrogen or methyl, and both  $R^2$  and  $R^5$  are 2,6-diisopropylphenyl, and wherein X is BAF,  $SbF_6$ ,  $PF_6$ , or  $BF_4$ .

236. The compound as recited in claim 232 wherein X is  $BAF^-$ ,  $SbF_6^-$ ,  $PF_6^-$ , or  $BF_4^-$ .

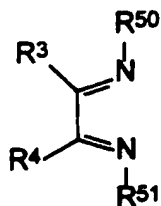
20 237. The compound as recited in claim 232 wherein  $R^2$  and  $R^5$  are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and  $R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, or  $R^3$  and  $R^4$  taken together are hydrocarbylene to form a carbocyclic ring.

25 238. The compound as recited in claim 232 wherein each of  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$ ,  $T^1$ , Z, and X are as follows:

R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	R <sup>5</sup>	T <sup>1</sup>	Z	X
2,6-i-PrPh	Me	Me	2,6-i-PrPh	Me	OEt <sub>2</sub>	BAF
2,6-i-PrPh	H	H	2,6-i-PrPh	Me	OEt <sub>2</sub>	BAF
2,6-MePh	H	H	2,6-MePh	Me	OEt <sub>2</sub>	BAF
2,6-MePh	Me	Me	2,6-MePh	Me	OEt <sub>2</sub>	BAF
2,6-i-PrPh	Me	Me	2,6-i-PrPh	Me	OEt <sub>2</sub>	SbF <sub>6</sub>
2,6-i-PrPh	Me	Me	2,6-i-PrPh	Me	OEt <sub>2</sub>	BF <sub>4</sub>
2,6-i-PrPh	Me	Me	2,6-i-PrPh	Me	OEt <sub>2</sub>	PF <sub>6</sub>
2,6-i-PrPh	H	H	2,6-i-PrPh	Me	OEt <sub>2</sub>	SbF <sub>6</sub>
2,4,6-MePh	Me	Me	2,4,6-MePh	Me	OEt <sub>2</sub>	SbF <sub>6</sub>
2,6-i-PrPh	An	An	2,6-i-PrPh	Me	OEt <sub>2</sub>	SbF <sub>6</sub>
2,6-i-PrPh	Me	Me	2,6-i-PrPh	Me	NCMe	SbF <sub>6</sub>
Ph	Me	Me	Ph	Me	NCMe	SbF <sub>6</sub>
2,6-EtPh	Me	Me	2,6-EtPh	Me	NCMe	BAF
2,6-EtPh	Me	Me	2,6-EtPh	Me	NCMe	SbF <sub>6</sub>
2-t-BuPh	Me	Me	2-t-BuPh	Me	NCMe	SbF <sub>6</sub>
1-Np	Me	Me	1-Np	Me	NCMe	SbF <sub>6</sub>
Ph <sub>2</sub> CH	H	H	Ph <sub>2</sub> CH	Me	NCMe	SbF <sub>6</sub>
2-PhPh	Me	Me	2-PhPh	Me	NCMe	SbF <sub>6</sub>
Ph	a	a	Ph	Me	NCMe	BAF
Ph	Me	Me	Ph	Me	NCMe	SbF <sub>6</sub>
Ph	Ph	Ph	Ph	Me	NCMe	BAF
Ph <sub>2</sub> CH	H	H	Ph <sub>2</sub> CH	Me	NCMe	SbF <sub>6</sub>
Ph <sub>2</sub> CH	H	H	Ph <sub>2</sub> CH	Me	SMe <sub>2</sub>	SbF <sub>6</sub>

<sup>a</sup> -CMe<sub>2</sub>CH<sub>2</sub>CMe<sub>2</sub>-.

239. A compound of the formula



wherein:

5

R<sup>50</sup> is substituted phenyl;

R<sup>51</sup> is phenyl or substituted phenyl;



$R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or  $R^3$  and  $R^4$  taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

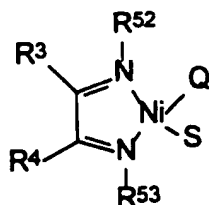
5 and provided that groups in the 2 and 6 positions of  $R^{50}$  have a difference in  $E_s$  of about 0.15 or more.

240. The compound as recited in claim 239 wherein groups in the 2 and 6 of  $R^{51}$  have a difference in  $E_s$  of about 0.60 or more.

10 241. The compound as recited in claim 239 wherein the group in the 2 position of  $R^{50}$  is t-butyl and the group in 6 position of  $R^{50}$  is methyl or hydrogen.

242. The compound as recited in claim 241 wherein the group in the 2 position of  $R^{51}$  is t-butyl and the  
15 group in 6 position of  $R^{51}$  is methyl or hydrogen.

243. A compound of the formula



(XXXVI)

20 wherein:

$R^{52}$  is substituted phenyl;

$R^{53}$  is phenyl or substituted phenyl;

$R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or  $R^3$  and  $R^4$  taken  
25 together are hydrocarbylene or substituted hydrocarbylene to form a ring;

$Q$  is alkyl, hydride, chloride, bromide or iodide;

$S$  is alkyl, hydride, chloride, bromide or  
30 iodide;

and provided that;

groups in the 2 and 6 positions of  $R^{52}$  have a difference in  $E_s$  of 0.15 or more; and

except when M is Pd, when both Q and S are each independently chloride, bromide or iodide W is capable of transferring a hydride or alkyl group to M.

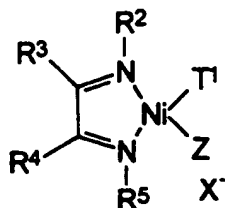
244. The compound as recited in claim 243 wherein  
5 said difference is about 0.20 more.

245. The compound as recited in claim 243 wherein groups in the 2 and 6 of  $R^{51}$  have a difference in  $E_s$  of 0.15 or more.

246. The compound as recited in claim 243 wherein  
10 the group in the 2 position of  $R^{52}$  is i-propyl or t-butyl and the group in the 6 position of  $R^{52}$  is methyl or hydrogen.

247. The compound as recited in claim 246 wherein  
15 the group in the 2 position of  $R^{53}$  is i-propyl or t-butyl and the group in 6 position of  $R^{52}$  is methyl or hydrogen.

248. A compound of the formula



20

(III)

wherein:

$R^2$  and  $R^5$  are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom  
25 bound to the imino nitrogen atom has at least two carbon atoms bound to it;

$R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or  $R^3$  and  $R^4$  taken together are hydrocarbylene or substituted  
30 hydrocarbylene to form a ring;

$T^1$  is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds,  $R^{15}C(=O)-$  or  $R^{15}OC(=O)-$ ;

$R^{15}$  is hydrocarbyl not containing an olefinic or acetylenic bond;

Z is a neutral Lewis base wherein the donating atom is nitrogen, sulfur or oxygen, provided that if  
 5 the donating atom is nitrogen then the pKa of the conjugate acid of that compound is less than about 6;

$X^-$  is a weakly coordinating anion.

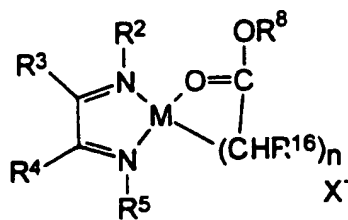
249. The compound as recited in claim 248 wherein  
 10  $T^1$  is methyl, Z is  $R^6_2O$  wherein each  $R^6$  is independently alkyl, and X is BAF,  $SbF_6$ ,  $PF_6$ , or  $BF_4$ .

250. The compound as recited in claim 248 wherein  
 $R^3$  and  $R^4$  are each independently hydrogen or methyl, and both  $R^2$  and  $R^5$  are 2,6-diisopropylphenyl.

251. The compound as recited in claim 249 wherein  
 15  $R^3$  and  $R^4$  are each independently hydrogen or methyl, and both  $R^2$  and  $R^5$  are 2,6-diisopropylphenyl.

252. The compound as recited in claim 248 wherein  
 $R^2$  and  $R^5$  are each independently hydrocarbyl provided that the carbon atom bound to the imino nitrogen atom  
 20 has at least two carbon atoms bound to it; and  $R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, or  $R^3$  and  $R^4$  taken together are hydrocarbylene to form a ring.

253. A compound of the formula  
 25



(IV)

wherein:

5         $R^2$  and  $R^5$  are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

$R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or  $R^3$  and  $R^4$  taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

10        M is Ni(II) or Pd(II);

      each  $R^{16}$  is independently hydrogen or alkyl containing 1 to 10 carbon atoms;

      n is 1, 2, or 3;

$X^-$  is a weakly coordinating anion; and

15         $R^8$  is hydrocarbyl.

      254. The compound as recited in claim 253 wherein  $R^3$  and  $R^4$  are each independently hydrogen or methyl, both  $R^2$  and  $R^5$  are 2,6-diisopropylphenyl, M is Pd(II), and X is BAF,  $SbF_6$ ,  $PF_6$ , or  $BF_4$ .

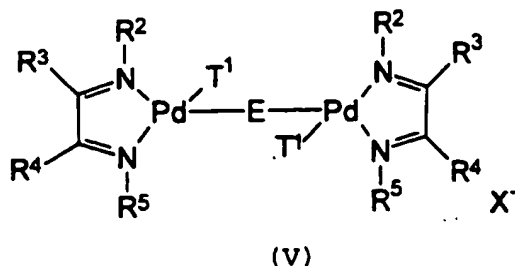
20        255. The compound as recited in claim 254 wherein each  $R^{16}$  is hydrogen and n is 3.

      256. The compound as recited in claim 253 wherein M is Pd(II).

25        257. The compound as recited in claim 253 wherein each  $R^{16}$  is hydrogen and n is 3.

      258. The compound as recited in claim 253 wherein  $R^2$  and  $R^5$  are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and  $R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, or  $R^3$  and  $R^4$  taken together are hydrocarbylene to form a ring.

30        259. A compound of the formula



wherein:

5            $R^2$  and  $R^5$  are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it;

10            $R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or  $R^3$  and  $R^4$  taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

          E is halogen or  $-OR^{18}$ ;

15            $R^{18}$  is hydrocarbyl not containing olefinic or acetylenic bonds;

$T^1$  is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds,  $R^{15}C(=O)-$  or  $R^{15}OC(=O)-$ ;

$R^{15}$  is hydrocarbyl not containing olefinic or acetylenic bonds; and

20            $X^-$  is a weakly coordinating anion.

260. The compound as recited in claim 259 wherein  $R^2$  and  $R^5$  are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and  $R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, or  $R^3$  and  $R^4$  taken together are hydrocarbylene to form a ring.

261. The compound as recited in claim 259 wherein  $T^1$  is methyl, and E is chlorine.

30           262. The compound as recited in claim 261 wherein  $R^3$  and  $R^4$  are each independently hydrogen or methyl, and both  $R^2$  and  $R^5$  are 2,6-diisopropylphenyl.

263. The compound as recited in claim 262 wherein  
X is BAF, SbF<sub>6</sub>, PF<sub>6</sub>, or BF<sub>4</sub>.

264. A compound of the formula  $[(\eta^4-1,5-$   
COD)PdT<sup>1</sup>Z]<sup>+</sup>X<sup>-</sup>, wherein:

5 T<sup>1</sup> is hydrocarbyl not containing olefinic or  
acetylenic bonds;

X<sup>-</sup> is a weakly coordinating anion;

COD is 1,5-cyclooctadiene;

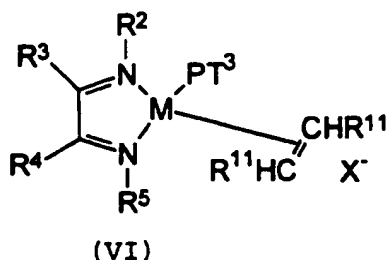
Z is R<sup>10</sup>CN; and

10 R<sup>10</sup> is hydrocarbyl not containing olefinic or  
acetylenic bonds.

265. The compound as recited in claim 264 wherein  
T<sup>1</sup> is methyl.

266. The compound as recited in claim 265 wherein  
15 Z is methyl and X is BAF, SbF<sub>6</sub>, PF<sub>6</sub>, or BF<sub>4</sub>.

267. A compound of the formula



20

wherein:

M is Ni(II) or Pd(II);

25 R<sup>2</sup> and R<sup>5</sup> are hydrocarbyl or substituted  
hydrocarbyl, provided that the carbon atom bound  
directly to the imino nitrogen atom has at least two  
carbon atoms bound to it;

30 R<sup>3</sup> and R<sup>4</sup> are each independently hydrogen,  
hydrocarbyl, substituted hydrocarbyl, or R<sup>3</sup> and R<sup>4</sup>  
taken together are hydrocarbylene or substituted  
hydrocarbylene to form a ring;

each R<sup>11</sup> is independently hydrogen, alkyl or  
- (CH<sub>2</sub>)<sub>m</sub>CO<sub>2</sub>R<sup>1</sup>;

$T^3$  is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, or  $-CH_2CH_2CH_2CO_2R^8$ ;

$P$  is a divalent group containing one or more repeat units derived from the polymerization of one or more of ethylene, an olefin of the formula  $R^{17}CH=CH_2$  or  $R^{17}CH=CHR^{17}$ , cyclobutene, cyclopentene, substituted norbornene, or norbornene and, when  $M$  is  $Pd(II)$ , optionally one or more of: a compound of the formula  $CH_2=CH(CH_2)_mCO_2R^1$ ,  $CO$ , or a vinyl ketone;

10  $R^8$  is hydrocarbyl;

$m$  is 0 or an integer from 1 to 16;

$R^1$  is hydrogen, or hydrocarbyl or substituted hydrocarbyl containing 1 to 10 carbon atoms;

and  $X^-$  is a weakly coordinating anion.

15 268. The compound as recited in claim 267 wherein  $R^1$  is hydrocarbyl or substituted hydrocarbyl.

269. The compound as recited in claim 267 wherein  $T^3$  is hydrogen or alkyl.

20 270. The compound as recited in claim 267 wherein  $M$  is  $Pd(II)$ .

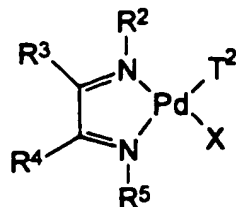
271. The compound as recited in claim 269 wherein  $M$  is  $Pd(II)$ .

272. The compound as recited in claim 267 wherein  $R^3$  and  $R^4$  are each independently hydrogen or methyl, and both  $R^2$  and  $R^5$  are 2,6-diisopropylphenyl.

273. The compound as recited in claim 271 wherein  $R^3$  and  $R^4$  are each independently hydrogen or methyl, and both  $R^2$  and  $R^5$  are 2,6-diisopropylphenyl.

274. The compound as recited in claim 267 wherein  $R^2$  and  $R^5$  are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and  $R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, or  $R^3$  and  $R^4$  taken together are hydrocarbylene to form a ring.

275. A compound of the formula



(VII)

wherein:

5           R<sup>2</sup> and R<sup>5</sup> are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

10           R<sup>3</sup> and R<sup>4</sup> are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or R<sup>3</sup> and R<sup>4</sup> taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

15           T<sup>2</sup> is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, hydrocarbyl substituted with keto or ester groups but not containing olefinic or acetylenic bonds, R<sup>15</sup>C(=O)- or R<sup>15</sup>OC(=O)-;

          R<sup>15</sup> is hydrocarbyl not containing olefinic or acetylenic bonds; and

          X is a weakly coordinating anion.

20           276. The compound as recited in claim 275 wherein T<sup>2</sup> is methyl.

25           277. The compound as recited in claim 276 wherein R<sup>3</sup> and R<sup>4</sup> are each independently hydrogen or methyl or R<sup>3</sup> and R<sup>4</sup> taken together are 1,8-naphthylylene, and both R<sup>2</sup> and R<sup>5</sup> are 2,6-diisopropylphenyl.

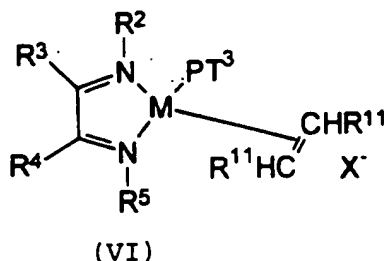
          278. The compound as recited in claim 276 wherein X is BAF, SbF<sub>6</sub>, PF<sub>6</sub>, or BF<sub>4</sub>.

30           279. The compound as recited in claim 275 wherein R<sup>2</sup> and R<sup>5</sup> are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and R<sup>3</sup> and R<sup>4</sup> are each independently hydrogen, hydrocarbyl, or R<sup>3</sup>



and R<sup>4</sup> taken together are hydrocarbylene to form a ring.

280. A process for the production of polyolefins, comprising, contacting, at a temperature of about -  
5 100°C to about +200°C, a compound of the formula



10 with one or more monomers selected from the group consisting of ethylene, an olefin of the formula R<sup>17</sup>CH=CH<sub>2</sub> or R<sup>17</sup>CH=CHR<sup>17</sup>, cyclobutene, cyclopentene, substituted norbornene, and norbornene,

wherein:

15 M is Ni(II) or Pd(II);

R<sup>2</sup> and R<sup>5</sup> are hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it;

20 R<sup>3</sup> and R<sup>4</sup> are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or R<sup>3</sup> and R<sup>4</sup> taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

each R<sup>11</sup> is independently hydrogen, alkyl or  
25 - (CH<sub>2</sub>)<sub>m</sub>CO<sub>2</sub>R<sup>1</sup>;

T<sup>3</sup> is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, or -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>R<sup>8</sup>;

P is a divalent group containing one or more repeat units derived from the polymerization of one or  
30 monomers selected from the group consisting of ethylene, an olefin of the formula R<sup>17</sup>CH=CH<sub>2</sub> or R<sup>17</sup>CH=CHR<sup>17</sup>, cyclopentene, cyclobutene, substituted norbornene, and norbornene, and, when M is Pd(II),

optionally one or more of: a compound of the formula  
 $\text{CH}_2=\text{CH}(\text{CH}_2)_m\text{CO}_2\text{R}^1$ , CO, or a vinyl ketone;

$\text{R}^8$  is hydrocarbyl;

each  $\text{R}^{17}$  is independently hydrocarbyl or  
5 substituted hydrocarbyl provided that any olefinic bond  
in said olefin is separated from any other olefinic  
bond or aromatic ring by a quaternary carbon atom or at  
least two saturated carbon atoms;

$\text{R}^1$  is hydrogen, or hydrocarbyl or substituted  
10 hydrocarbyl containing 1 to 10 carbon atoms;

$m$  is 0 or an integer of 1 to 16;

and  $X$  is a weakly coordinating anion;

provided that when norbornene or substituted  
norbornene is present no other monomer is present;

15 when  $M$  is Pd a diene is not present; and

further provided that when  $M$  is Ni(II)  $\text{R}^{11}$  is not  
 $-\text{CO}_2\text{R}^8$ .

281. The compound as recited in claim 280 wherein  
 $\text{R}^2$  and  $\text{R}^5$  are each independently hydrocarbyl, provided  
20 that the carbon atom bound to the imino nitrogen atom  
has at least two carbon atoms bound to it; and  $\text{R}^3$  and  
 $\text{R}^4$  are each independently hydrogen, hydrocarbyl, or  $\text{R}^3$   
and  $\text{R}^4$  taken together are hydrocarbylene to form a  
ring; and each  $\text{R}^{17}$  is hydrocarbyl.

25 282. The process as recited in claim 280 wherein  
 $\text{T}^3$  is methyl.

283. The process as recited in claim 282 wherein  
said monomer is ethylene only, and  $\text{R}^{11}$  is hydrogen.

30 284. The process as recited in claim 282 wherein  
said monomer is an  $\alpha$ -olefin only, and  $\text{R}^{11}$  is alkyl.

285. The process as recited in claim 284 wherein  
said  $\alpha$ -olefin is propylene, and  $\text{R}^{11}$  is methyl.

286. The process as recited in claim 280 wherein  $M$   
is Pd(II), and one or more comonomers selected from the  
35 group consisting of: a compound of the formula  
 $\text{CH}_2=\text{CH}(\text{CH}_2)_m\text{CO}_2\text{R}^1$ , wherein  $\text{R}^1$  is hydrogen or, hydrocarbyl  
or substituted hydrocarbyl containing 1 to 10 carbon

atoms, and m is 0 or an integer of 1 to 16; CO; and a vinyl ketone is also present.

287. The process as recited in claim 286 wherein m is 0, and R<sup>1</sup> is hydrocarbyl or substituted hydrocarbyl.

5 288. The process as recited in claim 287 wherein m is 0, and R<sup>1</sup> is hydrocarbyl or substituted hydrocarbyl.

289. The process as recited in claim 280 done in the presence of a solvent.

10 290. The process as recited in claim 280 done in the absence of a solvent.

291. The process as recited in claim 282 wherein R<sup>3</sup> and R<sup>4</sup> are each independently hydrogen or methyl or R<sup>3</sup> and R<sup>4</sup> taken together are 1,8-naphthylidene, and both R<sup>2</sup> and R<sup>5</sup> are 2,6-diisopropylphenyl.

15 292. The process as recited in claim 280 used to make a block polymer.

293. The process as recited in claim 280 wherein X is BAF, SbF<sub>6</sub>, PF<sub>6</sub>, or BF<sub>4</sub>.

20 294. The process as recited in claim 291 wherein X is BAF, SbF<sub>6</sub>, PF<sub>6</sub>, or BF<sub>4</sub>.

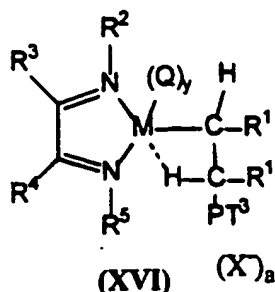
295. The process as recited in claim 294 wherein a monomer is ethylene or propylene.

296. The process as recited in claim 280 wherein the monomers are ethylene and propylene.

25 297. The process as recited in claim 280 wherein said monomers are part of a crude butenes stream.

298. The process as recited in claim 280 wherein said monomers comprise cyclopentene.

30 299. A process for the production of polyolefins, comprising, contacting, at a temperature of about -100°C to about +200°C, a compound of the formula



and one or more monomers selected from the group consisting of ethylene, an olefin of the formula  
 5  $R^{17}CH=CH_2$  or  $R^{17}CH=CHR^{17}$ , cyclobutene, cyclopentene, substituted norbornene, and norbornene,

wherein:

M is Zr, Ti, Sc, V, Cr, a rare earth metal, Fe, Co, Ni or Pd of oxidation state m;

10  $R^2$  and  $R^5$  are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it;

$R^3$  and  $R^4$  are each independently hydrogen,  
 15 hydrocarbyl, substituted hydrocarbyl, or  $R^3$  and  $R^4$  taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

each  $R^{11}$  is independently hydrogen or alkyl, or both of  $R^{11}$  taken together are hydrocarbylene to form a  
 20 carbocyclic ring;

$T^3$  is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, or  $-CH_2CH_2CH_2CO_2R^8$ ; Q is a monoanion;

P is a divalent group containing one or more  
 25 repeat units derived from the polymerization of one or monomers selected from the group consisting of ethylene, an olefin of the formula  $R^{17}CH=CH_2$  or  $R^{17}CH=CHR^{17}$ , cyclopentene, cyclobutene, substituted norbornene, and norbornene, and, when M is Pd(II),  
 30 optionally one or more of: a compound of the formula  $CH_2=CH(CH_2)_mCO_2R^1$ , CO, or a vinyl ketone;

$R^8$  is hydrocarbyl;

a is 1 or 2;

$y + a + 1 = m$ ;

each  $R^{17}$  is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

$R^1$  is hydrogen, or hydrocarbyl or substituted hydrocarbyl containing 1 to 10 carbon atoms;

m is 0 or an integer of 1 to 16;

and X is a weakly coordinating anion;

provided that, when norbornene or substituted norbornene is present, no other monomer is present;

when M is Pd a diene is not present; and

further provided that, when M is Ni(II),  $T^3$  is not  $-CH_2CH_2CH_2CO_2R^8$ .

300. The process as recited in claim 299 wherein  $R^2$  and  $R^5$  are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and  $R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, or  $R^3$  and  $R^4$  taken together are hydrocarbylene to form a ring; and each  $R^{17}$  is hydrocarbyl.

301. The process as recited in claim 299 wherein  $T^3$  is methyl.

302. The process as recited in claim 301 wherein said monomer is ethylene only, and  $R^{11}$  is hydrogen.

303. The process as recited in claim 301 wherein said monomer is an  $\alpha$ -olefin only, and  $R^{11}$  is alkyl.

304. The process as recited in claim 303 wherein said  $\alpha$ -olefin is propylene, and each  $R^{11}$  is methyl or hydrogen.

305. The process as recited in claim 299 wherein M is Pd(II), and one or more comonomer selected from the group consisting of: a compound of the formula  $CH_2=CH(CH_2)_mCO_2R^1$ , wherein  $R^1$  is hydrogen or, hydrocarbyl or substituted hydrocarbyl containing 1 to 10 carbon

atoms, and m is 0 or an integer of 1 to 16; CO; and a vinyl ketone is also present.

306. The process as recited in claim 305 wherein m is 0, and R<sup>1</sup> is hydrocarbyl or substituted hydrocarbyl.

5 307. The process as recited in claim 299 done in the presence of a solvent.

308. The process as recited in claim 299 done in the absence of a solvent.

309. The process as recited in claim 301 wherein  
10 R<sup>3</sup> and R<sup>4</sup> are each independently hydrogen or methyl, and both R<sup>2</sup> and R<sup>5</sup> are 2,6-diisopropylphenyl.

310. The process as recited in claim 299 used to make a block polymer.

311. The process as recited in claim 299 wherein X  
15 is BAF, SbF<sub>6</sub>, PF<sub>6</sub>, or BF<sub>4</sub>.

312. The process as recited in claim 309 wherein X is BAF, SbF<sub>6</sub>, PF<sub>6</sub>, or BF<sub>4</sub>.

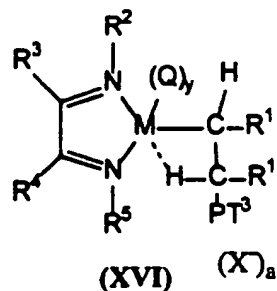
313. The process as recited in claim 312 wherein a monomer is ethylene or propylene.

20 314. The process as recited in claim 299 wherein the monomers are ethylene and propylene.

315. The process as recited in claim 299 wherein said monomers are part of a crude butenes stream.

316. The process as recited in claim 299 wherein  
25 said monomer comprises cyclopentene.

317. A compound of the formula



30 wherein:

M is Zr, Ti, Sc, V, Cr, a rare earth metal, Fe, Co, Ni or Pd of oxidation state m;

$R^2$  and  $R^5$  are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it;

5  $R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or  $R^3$  and  $R^4$  taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

10 each  $R^{11}$  is independently hydrogen, or alkyl, or both of  $R^{11}$  taken together are hydrocarbylene to form a carbocyclic ring;

$T^3$  is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, or  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{R}^8$ ;

15 P is a divalent group containing one or more repeat units derived from the polymerization of one or monomers selected from the group consisting of ethylene, an olefin of the formula  $\text{R}^{17}\text{CH}=\text{CH}_2$  or  $\text{R}^{17}\text{CH}=\text{CHR}^{17}$ , cyclopentene, cyclobutene, substituted norbornene, and norbornene, and optionally, when M is  
20  $\text{Pd(II)}$ , one or more of: a compound of the formula  $\text{CH}_2=\text{CH}(\text{CH}_2)_m\text{CO}_2\text{R}^1$ , CO, or a vinyl ketone;

Q is a monovalent anion;

$\text{R}^8$  is hydrocarbyl;

a is 1 or 2;

25  $y + a + 1 = m$ ;

each  $\text{R}^{17}$  is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at  
30 least two saturated carbon atoms;

$\text{R}^1$  is hydrogen, or hydrocarbyl or substituted hydrocarbyl containing 1 to 10 carbon atoms;

m is 0 or an integer of 1 to 16; and

and X is a weakly coordinating anion;

35 and provided that when M is Pd a diene is not present;.

318. The compound as recited in claim 317 wherein  $\text{R}^1$  is hydrocarbyl or substituted hydrocarbyl.

319. The compound as recited in claim 317 wherein  $T^3$  is hydrogen or alkyl.

320. The compound as recited in claim 317 wherein  $R^2$  and  $R^5$  are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and  $R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, or  $R^3$  and  $R^4$  taken together are hydrocarbylene to form a ring; and each  $R^{17}$  is hydrocarbyl.

321. The compound as recited in claim 317 wherein M is Pd(II).

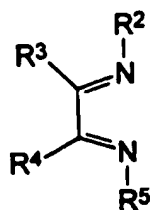
322. The compound as recited in claim 319 wherein M is Pd(II).

323. The compound as recited in claim 317 wherein  $R^3$  and  $R^4$  are each independently hydrogen or methyl, and both  $R^2$  and  $R^5$  are 2,6-diisopropylphenyl.

324. The compound as recited in claim 317 wherein both of  $R^{11}$  taken together form a five-membered carbocyclic ring.

325. The compound as recited in claim 317 wherein both of  $R^{11}$  taken together are hydrocarbylene to form a carbocyclic ring.

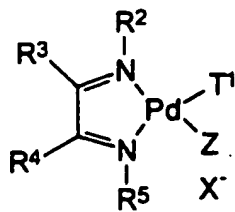
326. A process, comprising, contacting, at a temperature of about  $-40^\circ\text{C}$  to about  $+60^\circ\text{C}$ , a compound of the formula  $[(\eta^4-1,5\text{-COD})\text{Pd}T^1Z]^+X^-$  and a diimine of the formula



30

to produce a compound of the formula





(II)

wherein:

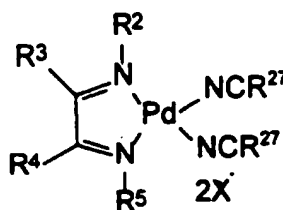
- 5           T<sup>1</sup> is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, R<sup>15</sup>C(=O)- or R<sup>15</sup>OC(=O)-; X is a weakly coordinating anion; COD is 1,5-cyclooctadiene; Z is R<sup>10</sup>CN;
- 10           R<sup>10</sup> is hydrocarbyl not containing olefinic or acetylenic bonds; R<sup>15</sup> is hydrocarbyl not containing olefinic or acetylenic bonds; R<sup>2</sup> and R<sup>5</sup> are each independently hydrocarbyl or
- 15           substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and R<sup>3</sup> and R<sup>4</sup> are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or R<sup>3</sup> and R<sup>4</sup>
- 20           taken together are hydrocarbylene or substituted hydrocarbylene to form a ring.
327. The process as recited in claim 326 wherein R<sup>10</sup> is alkyl, and T<sup>1</sup> is methyl.
328. The process as recited in claim 326 carried
- 25           out in a solvent of the formula R<sup>10</sup>CN, wherein R<sup>10</sup> is hydrocarbyl not containing olefinic or acetylenic bonds.
329. The process as recited in claim 327 wherein R<sup>3</sup> and R<sup>4</sup> are each independently hydrogen or methyl,
- 30           and both R<sup>2</sup> and R<sup>5</sup> are 2,6-diisopropylphenyl.
330. The process as recited in claim 326 wherein X is BAF, SbF<sub>6</sub>, PF<sub>6</sub>, or BF<sub>4</sub>.

331. The process as recited in claim 326 wherein  
 $R^2$  and  $R^5$  are each independently hydrocarbyl, provided  
 that the carbon atom bound to the imino nitrogen atom  
 has at least two carbon atoms bound to it; and  $R^3$  and  
 5  $R^4$  are each independently hydrogen, hydrocarbyl, or  $R^3$   
 and  $R^4$  taken together are hydrocarbylene to form a  
 ring.

332. An ethylene homopolymer with a density of  
 0.86 g/ml or less.

10 333. The ethylene homopolymer as recited in claim  
 332 wherein said density is about 0.85 or less.

334. A compound of the formula



15

(XIV)

wherein:

20  $R^2$  and  $R^5$  are each independently hydrocarbyl or  
 substituted hydrocarbyl, provided that the carbon atom  
 bound to the imino nitrogen atom has at least two  
 carbon atoms bound to it;

$R^3$  and  $R^4$  are each independently hydrogen,  
 hydrocarbyl, substituted hydrocarbyl, or  $R^3$  and  $R^4$   
 25 taken together are hydrocarbylene or substituted  
 hydrocarbylene to form a ring;

each  $R^{27}$  is hydrocarbyl; and

each X is a weakly coordinating anion.

335. The compound as recited in claim 334 wherein  
 30  $R^2$  and  $R^5$  are each independently hydrocarbyl, provided  
 that the carbon atom bound to the imino nitrogen atom  
 has at least two carbon atoms bound to it; and  $R^3$  and  
 $R^4$  are each independently hydrogen, hydrocarbyl, or  $R^3$

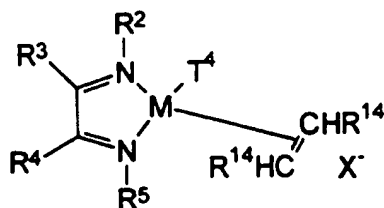
and R<sup>4</sup> taken together are hydrocarbylene to form a ring.

336. The compound as recited in claim 334 wherein both of R<sup>27</sup> are methyl.

5 337. The compound as recited in claim 334 wherein R<sup>3</sup> and R<sup>4</sup> are each independently hydrogen or methyl or R<sup>3</sup> and R<sup>4</sup> taken together are 1,8-naphthylidene, and both R<sup>2</sup> and R<sup>5</sup> are 2,6-diisopropylphenyl.

338. The compound as recited in claim 334 wherein 10 X is BAF, SbF<sub>6</sub>, PF<sub>6</sub>, or BF<sub>4</sub>.

339. A compound of the formula



15 (IX)

wherein:

M is Ni(II) or Pd(II);

20 R<sup>2</sup> and R<sup>5</sup> are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it;

25 R<sup>3</sup> and R<sup>4</sup> are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or R<sup>3</sup> and R<sup>4</sup> taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

each R<sup>14</sup> is independently hydrogen, alkyl or - (CH<sub>2</sub>)<sub>m</sub>CO<sub>2</sub>R<sup>1</sup>;

30 R<sup>1</sup> is hydrogen, or hydrocarbyl or substituted hydrocarbyl containing 1 to 10 carbon atoms;

T<sup>4</sup> is alkyl, -R<sup>60</sup>C(O)OR<sup>8</sup>, R<sup>15</sup>(C=O)- or R<sup>15</sup>OC(=O)-

;

$R^{15}$  is hydrocarbyl not containing olefinic or acetylenic bonds;

$R^{60}$  is alkylene not containing olefinic or acetylenic bonds;

5  $R^8$  is hydrocarbyl;;

and X is a weakly coordinating anion;

and provided that when  $R^{14}$  is  $-(CH_2)_mCO_2R^1$ , or  $T^4$  is not alkyl, M is Pd(II).

10 340. The compound as recited in claim 339 wherein  $R^2$  and  $R^5$  are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and  $R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, or  $R^3$  and  $R^4$  taken together are hydrocarbylene to form a  
15 ring.

341. The compound as recited in claim 339 wherein  $T^4$  is methyl and M is Pd(II).

342. The compound as recited in claim 339 wherein each  $R^{14}$  is independently hydrogen or  $-(CH_2)_mCO_2R^1$  and M  
20 is Pd(II).

343. A homopolypropylene with a glass transition temperature of  $-30^\circ\text{C}$  or less, provided that said homopolypropylene has at least 50 branches per 1000 methylene groups.

25 344. The homopolypropylene as recited in claim 343 wherein said glass transition temperature is about  $-35^\circ\text{C}$  or less.

345. A homopolymer of cyclopentene having a degree of polymerization of about 30 or more and an end of  
30 melting point of about  $100^\circ\text{C}$  to about  $320^\circ\text{C}$ , provided that said homopolymer has less than 5 mole percent of enchaind linear olefin containing pentylene units.

346. The homopolymer as recited in claim 345 wherein at least 90 percent of repeat units are 1,3-  
35 cyclopentylene repeat units.

347. The homopolymer as recited in claim 345 wherein at least 90 percent of repeat units are cis-1,3-cyclopentylene repeat units.

348. The homopolymer as recited in claim 345 wherein an X-ray powder diffraction pattern thereof has reflections at approximately  $17.3^\circ$ ,  $19.3^\circ$ ,  $24.2^\circ$ , and  $40.7^\circ$   $2\theta$ .

5        349. A homopolymer of cyclopentene that has an X-ray diffraction pattern with reflections at approximately  $17.3^\circ$ ,  $19.3^\circ$ ,  $24.2^\circ$ , and  $40.7^\circ$   $2\theta$ .

10        350. The homopolymer as recited in claim 349 which has a monoclinic unit cell of the approximate dimensions:  $a=0.561$  nm;  $b=0.607$  nm;  $c=7.37$  nm; and  $\beta=123.2^\circ$ .

351. The homopolymer as recited in claim 349 wherein at least 90 percent of repeat units are 1,3-cyclopentylene repeat units.

15        352. The homopolymer as recited in claim 351 wherein at least 90 percent of repeat units are cis-1,3-cyclopentylene repeat units.

20        353. A homopolymer of cyclopentene wherein at least 90 mole percent of enchaind cyclopentylene units are 1,3-cyclopentylene units, and said homopolymer has an average degree of polymerization of 30 more.

25        354. A homopolymer of cyclopentene wherein at least 90 mole percent of enchaind cyclopentylene units are cis-1,3-cyclopentylene, and said homopolymer has an average degree of polymerization of about 10 or more.

355. A copolymer of cyclopentene and ethylene wherein at least 75 mole percent of enchaind cyclopentylene units are 1,3-cyclopentylene units.

30        356. The copolymer as recited in claim 355 wherein at least 50 mole percent of the repeat units are derived from cyclopentene.

357. The copolymer as recited in claim 355 wherein there are at least 20 branches per 1000 methylene carbon atoms.

35        358. A copolymer of cyclopentene and ethylene wherein there are at least 20 branches per 1000 methylene carbon atoms.

359. The copolymer as recited in claim 358 wherein at least 50 mole percent of the repeat units are derived from ethylene.

360. A copolymer of cyclopentene and ethylene  
5 wherein at least 50 mole percent of the repeat units are derived from cyclopentene.

361. A copolymer comprising repeat units of cyclopentene and an  $\alpha$ -olefin.

362. The copolymer as recited in claim 361 wherein  
10 repeat units derived from ethylene are also present.

363. The copolymer as recited in claim 361 wherein said  $\alpha$ -olefin is a linear  $\alpha$ -olefin.

364. The copolymer as recited in claim 361 wherein at least 90 mole percent of repeat units derived from  
15 cyclopentene are 1,3-cyclopentylene units.

365. The copolymer as recited in claim 364 wherein at least 90 mole percent of repeat units derived from cyclopentene are cis-1,3-cyclopentylene units.

366. A fiber made from the polymer of claim 345,  
20 349, 353, 354, 355, 356, 357, 358, 360 or 361.

367. A polymerization process, comprising,  
contacting an olefin of the formula  $R^{17}CH=CH_2$  or  $R^{17}CH=CHR^{17}$ , each  $R^{17}$  is independently hydrogen,  
hydrocarbyl, or substituted hydrocarbyl provided that  
25 any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms with a catalyst, wherein said catalyst:

contains a nickel or palladium atom in a  
30 positive oxidation state;

contains a neutral bidentate ligand coordinated to said nickel or palladium atom, and wherein coordination to said nickel or palladium atom is through two nitrogen atoms or a nitrogen atom and a  
35 phosphorous atom; and

said neutral bidentate ligand, has an Ethylene Exchange Rate of less than  $20,000 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$  when said catalyst contains a palladium atom, and less than

50,000 L-mol<sup>-1</sup>s<sup>-1</sup> when said catalyst contains a nickel atom;

and provided that when M is Pd a diene is not present.

5 368. The polymerization process as recited in claim 367 wherein said Ethylene Exchange Rate is less than 10,000 L-mol<sup>-1</sup>s<sup>-1</sup> when said catalyst contains a palladium atom, and less than 25,000 L-mol<sup>-1</sup>s<sup>-1</sup> when said catalyst contains a nickel atom.

10 369. The process as recited in claim 367 wherein said bidentate ligand is coordinated to said nickel or palladium atom through two nitrogen atoms.

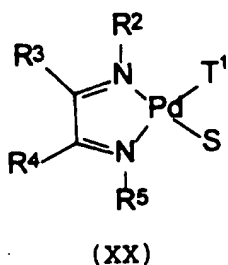
370. The process as recited in claim 369 wherein said ligand is an  $\alpha$ -diimine.

15 371. The process as recited in claim 367 wherein said olefin has the formula R<sup>17</sup>CH=CH<sub>2</sub>, wherein R<sup>17</sup> is hydrogen or n-alkyl.

20 372. A process for the polymerization of olefins, comprising, contacting, at a temperature of about -100°C to about +200°C:

a first compound which is a source of a relatively noncoordinating monoanion;

a second compound of the formula



30 and one or more monomers selected from the group consisting of ethylene, an olefin of the formula R<sup>17</sup>CH=CH<sub>2</sub>, or R<sup>17</sup>CH=CHR<sup>17</sup>, cyclobutene, cyclopentene, substituted norbornene, or norbornene; wherein:

$R^2$  and  $R^5$  are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

5  $R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or  $R^3$  and  $R^4$  taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

10 each  $R^{17}$  is independently hydrocarbyl or substituted hydrocarbyl provided that  $R^{17}$  does not contain any olefinic bonds;

$T^1$  is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds,  $R^{15}C(=O)-$  or  $R^{15}OC(=O)-$ ;

15  $S$  is chloride, iodide, or bromide; and provided that, when norbornene or substituted norbornene is present, no other monomer is present.

373. The process as recited in claim 372 wherein  $R^2$  and  $R^5$  are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom  
20 has at least two carbon atoms bound to it; and  $R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, or  $R^3$  and  $R^4$  taken together are hydrocarbylene to form a ring; and each  $R^{17}$  is saturated hydrocarbyl.

374. The process as recited in claim 372 wherein  
25 said source is an alkali metal salt of said anion.

375. The process as recited in claim 372 wherein  $T^1$  is methyl.

376. The process as recited in claim 372 wherein said monomer is ethylene only, and  $R^{11}$  is hydrogen.

30 377. The process as recited in claim 372 wherein one or more comonomer selected from the group consisting of: a compound of the formula

$CH_2=CH(CH_2)_mCO_2R^1$ , wherein  $R^1$  is hydrogen or, hydrocarbyl or substituted hydrocarbyl containing 1 to 10 carbon  
35 atoms, and  $m$  is 0 or an integer of 1 to 16; CO; and a vinyl ketone is also present.

378. The process as recited in claim 372 done in the presence of a solvent.



379. The process as recited in claim 368 used to make a block polymer.

380. The process as recited in claim 368 wherein said monoanion is  $\text{BAF}^-$ ,  $\text{SbF}_6^-$ ,  $\text{PF}_6^-$ , or  $\text{BF}_4^-$ .

5 381. The process as recited in claim 374 wherein said monoanion is  $\text{BAF}^-$ ,  $\text{SbF}_6^-$ ,  $\text{PF}_6^-$ , or  $\text{BF}_4^-$ .

382. The process as recited in claim 377 wherein a monomer is ethylene or propylene.

10 383. The process as recited in claim 372 wherein the monomers are ethylene and propylene.

384. A polyolefin, comprising, a polymer made by polymerizing one or more monomers of the formula  $\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_e\text{G}$  by contacting said monomers with a transition metal containing coordination polymerization catalyst, wherein:

each G is independently hydrogen or  $-\text{CO}_2\text{R}^1$ ;

each e is independently 0 or an integer of 1 to 20;

each  $\text{R}^1$  is independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

and provided that:

said polymer has at least 50 branches per 1000 methylene groups;

25 in at least 50 mole percent of said monomers G is hydrogen;

except when no branches should be theoretically present, the number of branches per 1000 methylene groups is 90% or less than the number of theoretical branches per 1000 methylene groups, or the number of branches per 1000 methylene groups is 110% or more of theoretical branches per 1000 methylene groups; and

30 when there should be no branches theoretically present, said polyolefin has 50 or more branches per 1000 methylene groups;

35 and provided that said polyolefin has at least two branches of different lengths containing less than 6 carbon atoms each.

385. The polyolefin as recited in claim 384 wherein except when no branches should be theoretically present the number of branches per 1000 methylene groups is 80% or less than the number of theoretical branches per 1000 methylene groups, or the number of branches per 1000 methylene groups is 120% or more of theoretical branches per 1000 methylene groups; and when there should be no branches theoretically present, said polyolefin has 75 or more branches per 1000 methylene groups.

386. A polyolefin, comprising, a polymer made by polymerizing one or more monomers of the formula  $H_2C=CH(CH_2)_eG$  by contacting said monomers with a transition metal containing coordination polymerization catalyst, wherein:

each G is independently hydrogen or  $-CO_2R^1$ ;  
each e is independently 0 or an integer of 1 to

20;

$R^1$  is independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

and provided that:

said polymer has at least 50 branches per 1000 methylene groups;

in at least 50 mole percent of said monomers G is hydrogen;

said polymer has at least 50 branches of the formula  $-(CH_2)_fG$  per 1000 methylene groups, wherein when G is the same as in a monomer and  $e \neq f$ , and/or for any single monomer of the formula  $H_2C=CH(CH_2)_eG$  there are less than 90% of the number of theoretical branches per 1000 methylene groups, or more than 110% of the theoretical branches per 1000 methylene groups of the formula  $-(CH_2)_fG$  and  $f=e$ , and wherein f is 0 or an integer of 1 or more;

and provided that said polyolefin has at least two branches of different lengths containing less than 6 carbon atoms each.

387. The polyolefin as recited in claim 386 wherein when G is the same as in a monomer and  $e \neq f$ , and/or for any single monomer of the formula  $H_2C=CH(CH_2)_eG$  there are less than 80% of the number of theoretical branches per 1000 methylene groups, or more than 120% of the theoretical branches per 1000 methylene groups of the formula  $-(CH_2)_fG$  and  $f=e$ .

388. A tackifier for an adhesive comprising the polymer of claim 1, 2, 3, 5, 6 or 7.

389. An oil additive for smoke suppression in two-stroke gasoline engines comprising the polymer of claim 1, 2, 3, 4, 5, 6, or 7.

390. A base resin for a hot melt adhesive, a pressure sensitive adhesive or a solvent applied adhesive comprising the polymer of claim 1, 2, 3, 4, 5, 6 or 7.

391. A viscosity modifier for lubricating oils comprising the polymer of claim 1, 2, 3, 4, 5, 6 or 7.

392. A coating or penetrant comprising the polymer of claim 1, 2, 4, 5, 6 or 7.

393. A base polymer for caulking comprising the polymer of claim 1, 2, 3, 4, 5, 6 or 7.

394. The polymer of claim 1, 2, 4, 5, 6 or 7 which is grafted so it contains functional groups.

395. A toughener for a thermoplastic or a thermoset comprising the polymer of claim 14.

396. A modifier for asphalt comprising the polymer of claim 1, 3, 4, 6, 7, 332 or 343.

397. The polymer of claim 1, 3, 4, 6, 7, 332 or 343 which is chlorinated or chlorosulfonated.

398. The polymer of claim 17 which is elastomeric.

399. A wire insulation or jacketing comprising the polymer of claim 1, 3, 4, 6, 7, 332 or 343.

400. A toughener for polyolefins comprising the polymer of claim 1, 3, 4, 6, 7, 332 or 343.

401. A base for a synthetic lubricant comprising the polymer of claim 1, 4, 6, 7, 332 or 343.

402. A drip suppressant for synthetic polymers comprising the polymer of claim 1, 3, 4, 6, 7, 332 or 343.

5 403. A blown or cast film, or a sheet comprising the polymer of claim 1, 3, 4, 6, 7, 332 or 343.

404. An additive for wax candles for smoke suppression or drip control comprising the polymer of claim 1, 4, 6, 7, 332 or 343.

10 405. A base resin for carpet backing comprising the polymer of claim 1, 3, 4, 6, 7, 332 or 343.

406. A capliner resin comprising the polymer of claim 1, 3, 4, 6, 7, 332 or 343.

407. A thermal transfer imaging resin comprising the polymer of claim 1, 4, 6, 7, 332 or 343.

15 408. An extrusion or coextrusion onto a plastic, metal, textile or paper web comprising the polymer of claim 1, 3, 4, 6, 7, 332 or 343.

409. A laminating adhesive for glass comprising the polymer of claim 1, 3, 4, 6, 7, 332 or 343.

20 410. A foamed object comprising the polymer of claim 1, 3, 4, 6, 7, 332 or 343.

411. A powder used to coat an object comprising the polymer of claim 1, 3, 4, 6, 7, 332 or 343.

25 412. A hose comprising the polymer of claim 1, 3, 4, 6, 7, 332 or 343.

413. A pour point depressant for a fuel or oil comprising the polymer of claim 1, 3, 4, 6, 7, 332 or 343.

30 414. A nonwoven fabric comprising the polymer of claim 1, 3, 4, 6, 7, 332 or 343.

415. A roofing membrane comprising the polymer of claim 1, 3, 4, 6, 7, 332 or 343.

416. A reactive diluent for an automotive finish comprising the polymer of claim 7, 8, 9, 10, 11 or 12.

35 417. An ionomer comprising the polymer of claim 7, 8, 9, 10, 11 or 12.

418. A molding resin comprising the ionomer of claim 417.

419. A core for the initiation of condensation polymerizations yielding a grafted branched polymer, comprising the polymer of claim 7, 8, 9, 10, 11, or 12.

420. A compatibilizing agent comprising the polymer  
5 of claim 3, 6 or 7.

421. A toughener for a thermoplastic or thermoset comprising the polymer of claim 1, 3, 4, 6, 7, 332 or 343.

422. An internal plasticizer for polymers  
10 comprising the polymer of claim 1, 3, 4, 6, 7, 332 or 343.

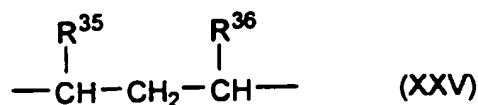
423. An adhesive for adhering a polymer comprising the polymer of claim 3, 6, 7, 332 or 343.

424. A curing agent for a polymer containing  
15 complimentary functional groups comprising the polymer of claim 3, 6 or 7.

425. An additive to thermoplastic polymers to improve the adhesion of paint thereto comprising the polymer of claim 3, 6 or 7.

426. A polymer blend comprising the polymer of  
20 claim 1, 3, 4, 6, 7, 332 or 343 and at least one other polymer.

427. A polymer of one or more alpha-olefins of the formula  $\text{CH}_2=\text{CH}(\text{CH}_2)_a\text{H}$  wherein a is an integer of 2 or  
25 more, which contains the structure



wherein  $\text{R}^{35}$  is an alkyl group and  $\text{R}^{36}$  is an alkyl group  
30 containing two or more carbon atoms, and provided that  $\text{R}^{35}$  is methyl in at least about 2 mole percent of the total amount of (XXV) in said polymer.

428. The polymer as recited in claim 427 wherein a structure in which  $\text{R}^{35}$  is methyl is about 5 mole  
35 percent or more of the total amount of (XXV) in said polymer.

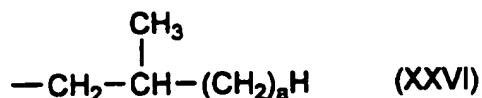
429. The polymer as recited in claim 427 wherein a structure in which R<sup>35</sup> is methyl is about 50 mole percent or more of the total amount of (XXV) in said polymer.

5        430. A polymer of one or more alpha-olefins of the formula  $\text{CH}_2=\text{CH}(\text{CH}_2)_a\text{H}$  wherein a is an integer of 2 or more, wherein said polymer contains methyl branches and said methyl branches are about 25 to about 75 mole percent of the total branches in said polymer.

10       431. The polymer as recited in claim 430 which contains branches of the formula  $-(\text{CH}_2)_a\text{H}$ .

432. The polymer as recited in claim 430 which contains branches of the formula  $-(\text{CH}_2)_n\text{H}$  wherein n is an integer of 6 or greater.

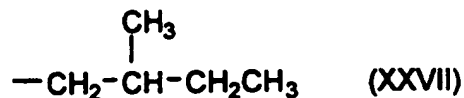
15       433. The polymer as recited in claim 431 which contains the structure



20       and wherein (XXVI) is present in an amount of 0.5 branches of (XXVI) or more per 1000 methylene atoms greater than can be accounted for by end groups.

434. A polyethylene containing the structure (XXVII) in an amount greater than can be accounted for by end groups.

25



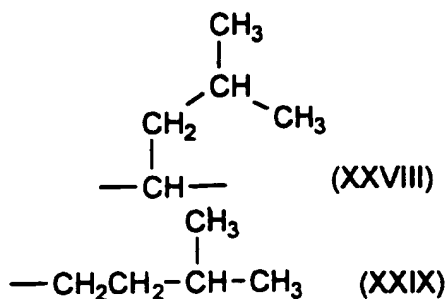
30       435. The polyethylene as recited in claim 434 which contains about 2 or more of (XXVII) per 1000 methylene groups in said polymer.

436. A polypropylene containing one or both of the structures (XXVIII) and (XXIX), provided that:

(XXIX), if present is present in an amount greater than or equal to 0.5 of (XXIX) per 1000

methylene groups greater than can be accounted for by end groups;

or the polymer contains at least 0.5 or more of (XXVIII) per 1000 methylene groups, if (XXVIII) is present.



437. The polypropylene as recited in claim 436 which contains about 15 or more groups of structure (XXVIII) per 1000 methylene groups in said polypropylene.

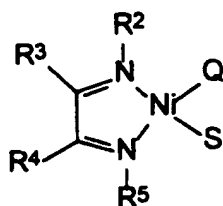
438. The polypropylene as recited in claim 436 which contains about 15 or more groups of structure (XXIX) per 1000 methylene groups in said polypropylene.

439. A process for the formation of linear  $\alpha$ -olefins, comprising, contacting, at a temperature of about  $-100^\circ\text{C}$  to about  $+200^\circ\text{C}$ :

ethylene;

a first compound W, which is a neutral Lewis acid capable of abstracting  $\text{X}^-$  to form  $\text{WX}^-$ , provided that the anion formed is a weakly coordinating anion, or a cationic Lewis or Bronsted acid whose counterion is a weakly coordinating anion; and

a second compound of the formula



(XXXI)

wherein:

$R^2$  and  $R^5$  are each independently hydrocarbyl or substituted hydrocarbyl;

$R^3$  and  $R^4$  are each independently hydrogen, substituted hydrocarbyl, hydrocarbyl, or  $R^3$  and  $R^4$  taken together are hydrocarbylene or substituted hydrocarbylene to form a ring; and

Q and S are each independently chlorine, bromine, iodine or alkyl; and

wherein an  $\alpha$ -olefin containing 4 to 40 carbon atoms is produced.

440. The process as recited in claim 439 wherein said linear  $\alpha$ -olefin has the formula  $H_2C=CHR^1$ , wherein  $R^1$  is n-alkyl containing 2 to 30 carbon atoms.

441. The process as recited in claim 439 wherein  $R^2$  and  $R^5$  are phenyl.

442. The process as recited in claim 439 wherein  $R^3$  and  $R^4$  are hydrogen, methyl or 1,8-naphthylylene.

443. The process as recited in claim 440 wherein  $R^3$  and  $R^4$  are hydrogen, methyl or 1,8-naphthylylene.

444. The process as recited in claim 439 wherein said second compound is an alkyl aluminum compound.

445. The process as recited in claim 444 wherein said alkyl aluminum compound is  $R^9Al$ ,  $R^9AlCl$ ,  $R^9AlCl_2$ ,  $R^9Al_2Cl_3$ , or  $R^9AlO$ , wherein  $R^9$  is alkyl containing 1 to 25 carbon atoms.

446. The process as recited in claim 445 wherein  $R^9$  contains 1 to 4 carbon atoms.

447. The process as recited in claim 443 wherein said second compound is  $R^9Al$ ,  $R^9AlCl$ ,  $R^9AlCl_2$ , or  $R^9AlO$ ,  $R^9Al_2Cl_3$ , wherein  $R^9$  is alkyl containing 1 to 25 carbon atoms.

448. The process as recited in claim 439 carried out at a temperature of about  $25^\circ C$  to about  $100^\circ C$ .

449. The process as recited in claim 439 wherein a partial pressure of said ethylene is about atmospheric pressure to about 275 MPa.

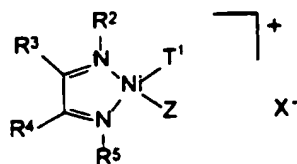
450. The process as recited in claim 439 wherein  $R^2$  and  $R^5$  are each independently hydrocarbyl, provided



that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and R<sup>3</sup> and R<sup>4</sup> are each independently hydrogen, hydrocarbyl, or R<sup>3</sup> and R<sup>4</sup> taken together are hydrocarbylene to form a ring.

451. A process for the formation of linear  $\alpha$ -olefins, comprising, contacting, at a temperature of about -100°C to about +200°C:

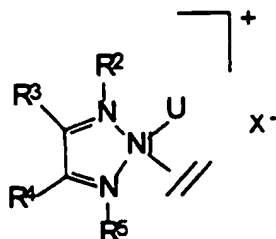
ethylene and a compound of the formula



10

(III)

or



15

(XXXIV)

wherein:

R<sup>2</sup> and R<sup>5</sup> are each independently hydrocarbyl or substituted hydrocarbyl;

R<sup>3</sup> and R<sup>4</sup> are each independently hydrogen, substituted hydrocarbyl, hydrocarbyl, or R<sup>3</sup> and R<sup>4</sup> taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

T<sup>1</sup> is hydrogen or n-alkyl containing up to 38 carbon atoms;

Z is a neutral Lewis base wherein the donating atom is nitrogen, sulfur, or oxygen, provided that if the donating atom is nitrogen then the pKa of the

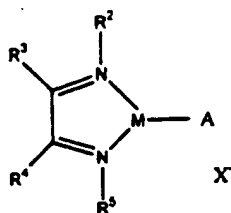
conjugate acid of that compound (measured in water) is less than about 6;

U is n-alkyl containing up to 38 carbon atoms;  
and

5 X is a noncoordinating anion;

and wherein an  $\alpha$ -olefin containing 4 to 40 carbon atoms is produced.

452. A process for the production of polyolefins, comprising, contacting, at a temperature of about 0°C  
10 to about +200°C, a compound of the formula.



XXXVII

and one or more monomers selected from the group  
15 consisting of ethylene, an olefin of the formula  $R^{17}CH=CH_2$  or  $R^{17}CH=CHR^{17}$ , cyclobutene, cyclopentene, substituted norbornene, and norbornene,

wherein:

20 M is Ni(II) or Pd(II);

A is a  $\pi$ -allyl or  $\pi$ -benzyl group;

$R^2$  and  $R^5$  are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it;

25  $R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or  $R^3$  and  $R^4$  taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

30 each  $R^{17}$  is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at

least two saturated carbon atoms;  $R^1$  is hydrogen, or hydrocarbyl or substituted hydrocarbyl containing 1 to 10 carbon atoms;

and X is a weakly coordinating anion;

5 and provided that;

when norbornene or substituted norbornene is present, no other monomer is present; and

when M is Pd a diene is not present.

453. The process as recited in claim 452 wherein  
10 said temperature is about 20°C to about 100°C.

454. The process as recited in claim 452 wherein said olefin is ethylene or a linear  $\alpha$ -olefin.

455. The process as recited in claim 452 wherein said olefin is ethylene.

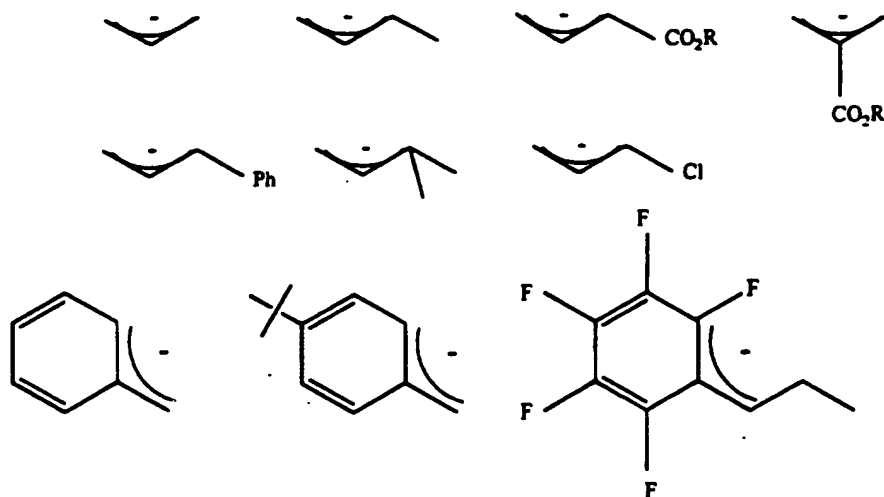
15 456. The process as recited in claim 452 wherein  $R^2$  and  $R^5$  are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and  $R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, or  $R^3$   
20 and  $R^4$  taken together are hydrocarbylene to form a ring.

457. The process as recited in claim 452 or 454 wherein a Lewis acid is also present.

458. The process as recited in claim 452 wherein M  
25 is Ni(II).

459. The process as recited in claim 452 wherein M is Pd(II).

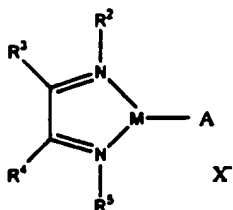
460. The process as recited in claim 452 wherein said  $\pi$ -allyl or  $\pi$ -benzyl group is selected from the  
30 group consisting of



wherein R is hydrocarbyl.

461. A compound of the formula

5



### XXXVII

wherein:

M is Ni(II) or Pd(II);

A is a  $\pi$ -allyl or  $\pi$ -benzyl group;

10  $\text{R}^2$  and  $\text{R}^5$  are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it;

$\text{R}^3$  and  $\text{R}^4$  are each independently hydrogen, 15 hydrocarbyl, substituted hydrocarbyl or  $\text{R}^3$  and  $\text{R}^4$  taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

each  $\text{R}^{17}$  is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at 20 least two saturated carbon atoms;  $\text{R}^1$  is hydrogen, or

hydrocarbyl or substituted hydrocarbyl containing 1 to 10 carbon atoms;

and X is a weakly coordinating anion;

and provided that when M is Pd a diene is not present.

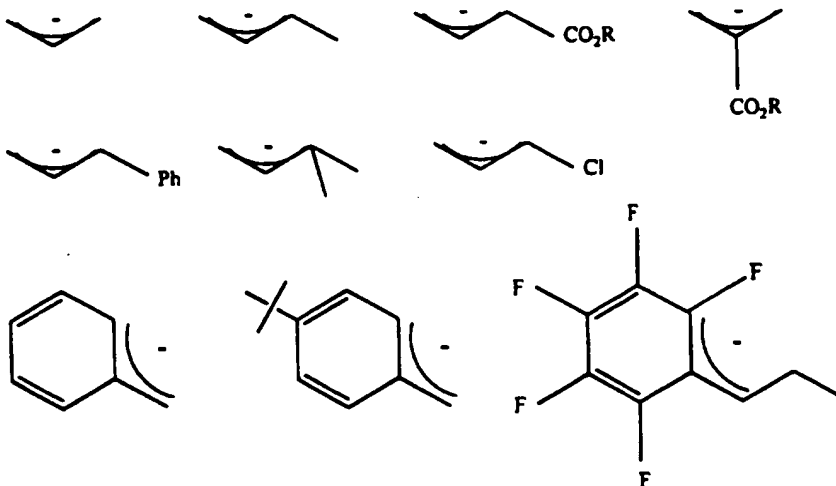
462. The compound as recited in claim 461 wherein  $R^2$  and  $R^5$  are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and  $R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, or  $R^3$  and  $R^4$  taken together are hydrocarbylene to form a ring.

463. The compound as recited in claim 461 wherein M is Ni(II).

464. The compound as recited in claim 461 wherein M is Pd(II).

465. The compound as recited in claim 461 wherein said  $\pi$ -allyl or  $\pi$ -benzyl group is selected from the group consisting of

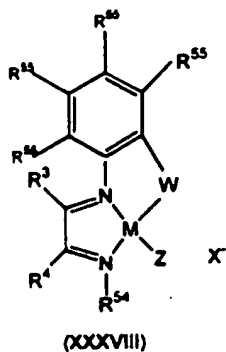
20



wherein R is hydrocarbyl.

466. A compound of the formula

25



wherein:

$R^3$  and  $R^4$  are each independently hydrogen,  
 5 hydrocarbyl, substituted hydrocarbyl or  $R^3$  and  $R^4$  taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

$R^{54}$  is hydrocarbyl or substituted hydrocarbyl,  
 provided that the carbon atom bound directly to the  
 10 imino nitrogen atom has at least two carbon atoms bound to it;

each  $R^{55}$  is independently hydrogen,  
 hydrocarbyl, substituted hydrocarbyl, or a functional  
 group;

15 W is alkylene or substituted alkylene containing 2 or more carbon atoms;

Z is a neutral Lewis base wherein the donating atom is nitrogen, sulfur, or oxygen, provided that if the donating atom is nitrogen then the pKa of the  
 20 conjugate acid of that compound (measured in water) is less than about 6, or an olefin of the formula  $R^{17}CH=CHR^{17}$ ;

each  $R^{17}$  is independently hydrogen, saturated hydrocarbyl or substituted saturated hydrocarbyl; and

25 X is a weakly coordinating anion;

and provided that when M is Ni, W is alkylene and each  $R^{17}$  is independently hydrogen or saturated hydrocarbyl.

467. The compound as recited in claim 466 wherein  
 30  $R^3$  and  $R^4$  are each independently hydrogen or

hydrocarbyl, or  $R^3$  and  $R^4$  taken together are hydrocarbylene to form a ring; and  $R^{54}$  is hydrocarbyl.

468. The compound as recited in claim 466 or 467 wherein each  $R^{55}$  is independently hydrogen or alkyl  
5 containing 1 to 10 carbon atoms.

469. The compound as recited in claim 466 wherein Z is neutral Lewis base.

470. The compound as recited in claim 469 wherein Z is a dialkyl ether.

10 471. The compound as recited in claim 466 wherein Z is  $R^{17}CH=CHR^{17}$ .

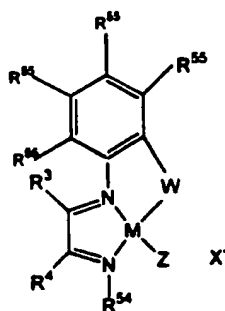
472. The compound as recited in claim 471 wherein each  $R^{17}$  is independently hydrogen or alkyl.

15 473. The compound as recited in claim 471 wherein both of  $R^{17}$  are hydrogen.

474. The compound as recited in claim 466 wherein W is  $-CH(CH_3)CH_2-$  or  $-C(CH_3)_2CH_2-$ .

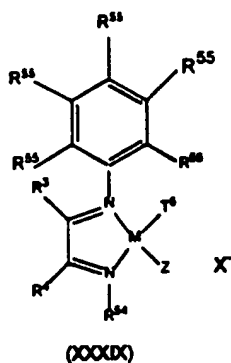
20 475. The compound as recited in claim 471 wherein W is a divalent polymeric radical derived from the polymerization of  $R^{17}CH=CHR^{17}$ .

476. A process for the production of a compound of the formula



(XXXVIII)

25 comprising, heating a compound of the formula



at a temperature of about  $-30^{\circ}\text{C}$  to about  $+100^{\circ}$  for a sufficient time to produce (XXXVIII), and wherein:

$\text{R}^3$  and  $\text{R}^4$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or  $\text{R}^3$  and  $\text{R}^4$  taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

$\text{R}^{54}$  is hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it;

each  $\text{R}^{55}$  is independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or a functional group;

$\text{R}^{56}$  is alkyl containing 2 to 30 carbon atoms;

$\text{T}^5$  is alkyl;

W is alkylene containing 2 to 30 carbon atoms;

Z is a neutral Lewis base wherein the donating atom is nitrogen, sulfur, or oxygen, provided that if the donating atom is nitrogen then the  $\text{pK}_a$  of the conjugate acid of that compound (measured in water) is less than about 6; and

X is a weakly coordinating anion.

477. The process as recited in claim 476 wherein  $\text{R}^3$  and  $\text{R}^4$  are each independently hydrogen or hydrocarbyl, or  $\text{R}^3$  and  $\text{R}^4$  taken together are hydrocarbylene to form a ring; and  $\text{R}^{54}$  is hydrocarbyl.

478. The process as recited in claim 476 or 472 wherein each  $\text{R}^{55}$  is independently hydrogen or alkyl containing 1 to 10 carbon atoms.

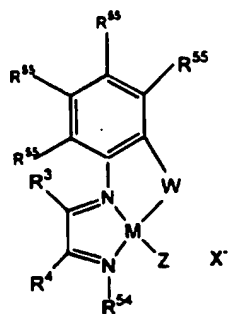


479. The process as recited in claim 476 wherein 2 is a dialkyl ether.

480. The process as recited in claim 476 wherein W is  $-\text{CH}(\text{CH}_3)\text{CH}_2-$  or  $-\text{C}(\text{CH}_3)_2\text{CH}_2-$

5 481. The process as recited in claim 476, 477, 479 or 480 wherein  $\text{T}^5$  is methyl.

482. A process for the polymerization of olefins, comprising, contacting a compound of the formula



(XXXVIII)

10 and one or more monomers selected from the group consisting of ethylene, an olefin of the formula  $\text{R}^{17}\text{CH}=\text{CH}_2$  or  $\text{R}^{17}\text{CH}=\text{CHR}^{17}$ , cyclobutene, cyclopentene, substituted norbornene, and norbornene,

15 wherein:

$\text{R}^3$  and  $\text{R}^4$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or  $\text{R}^3$  and  $\text{R}^4$  taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

20  $\text{R}^{54}$  is hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it;

each  $\text{R}^{55}$  is independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or a functional group;

W is alkylene or substituted alkylene containing 2 or more carbon atoms;

30 Z is a neutral Lewis base wherein the donating atom is nitrogen, sulfur, or oxygen, provided that if the donating atom is nitrogen then the pKa of the

conjugate acid of that compound (measured in water) is less than about 6, or an olefin of the formula  $R^{17}CH=CHR^{17}$ ;

each  $R^{17}$  is independently hydrogen, saturated hydrocarbyl or substituted saturated hydrocarbyl; and  
X is a weakly coordinating anion;  
and provided that:

when M is Ni, W is alkylene and each  $R^{17}$  is independently hydrogen or saturated hydrocarbyl;  
and when norbornene or substituted norbornene is present, no other monomer is present. 483. The process as recited in claim 482 wherein  $R^3$  and  $R^4$  are each independently hydrogen or hydrocarbyl, or  $R^3$  and  $R^4$  taken together are hydrocarbylene to form a ring; and  
 $R^{54}$  is hydrocarbyl.

484. The process as recited in claim 482 or 483 wherein each  $R^{55}$  is independently hydrogen or alkyl containing 1 to 10 carbon atoms.

485. The process as recited in claim 482 wherein Z is a dialkyl ether.

486. The process as recited in claim 482 wherein Z is  $R^{17}CH=CHR^{17}$ .

487. The process as recited in claim 482 wherein each  $R^{17}$  is independently saturated hydrocarbyl or hydrogen.

488. The process as recited in claim 482 wherein both of  $R^{17}$  are hydrogen.

489. The process as recited in claim 482 wherein W is  $-CH(CH_3)CH_2-$  or  $-C(CH_3)_2CH_2-$ .

490. The process as recited in claim 482 wherein said temperature is about 20°C to about 100°C.

491. The process as recited in claim 482 wherein said olefin is ethylene or a linear  $\alpha$ -olefin.

492. The process as recited in claim 482 wherein said olefin is ethylene, propylene or a combination of ethylene and propylene.

493. The process as recited in claim 486 wherein said olefin is ethylene, propylene or a combination of ethylene and propylene.

494. The process as recited in claim 489 wherein said olefin is cyclopentene.

495. The process as recited in claim 482 wherein said olefin is cyclopentene.

496. A homopolypropylene containing about 10 to about 700  $\Delta$ + methylene groups per 1000 methylene groups.

497. The homopolypropylene as recited in claim 496 containing about 25 to about 300  $\delta$ + methylene groups per 1000 methylene groups.

498. A homopolypropylene wherein a ratio of  $\delta$ +: $\gamma$  methylene groups is about 0.5 to about 7.

499. The homopolypropylene as recited in claim 498 wherein said ratio is about 0.7 to 2.0.

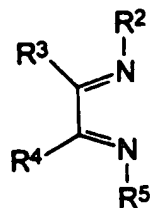
500. A homopolypropylene in which about 30 to about 85 mole percent of monomer units are enchaind in an  $\omega$ ,1 fashion.

501. The homopolypropylene as recited in claim 500 wherein about 30 to about 60 mole percent of the monomer units are enchaind in an  $\omega$ ,1 fashion.

502. A process for the formation of linear  $\alpha$ -olefins, comprising, contacting, at a temperature of about  $-100^{\circ}\text{C}$  to about  $+200^{\circ}\text{C}$ :

ethylene;

and a Ni[II] of



(VIII)

R<sup>2</sup> and R<sup>5</sup> are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom

bound to the imino nitrogen atom has at least two carbon atoms bound to it;

$R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or  $R^3$  and  $R^4$  taken together are hydrocarbylene or substituted hydrocarbylene to form a carbocyclic ring and wherein an  $\alpha$ -olefin containing 4 to 40 carbon atoms is produced.

503. The process as recited in claim 502 wherein said linear  $\alpha$ -olefin has the formula  $H_2C=CHR^1$ , wherein  $R^1$  is n-alkyl containing 2 to 30 carbon atoms.

504. The process as recited in claim 502 wherein  $R^2$  and  $R^5$  are phenyl.

505. The process as recited in claim 502 wherein  $R^3$  and  $R^4$  are hydrogen, methyl or 1,8-naphthylidene.

506. The process as recited in claim 503 wherein  $R^3$  and  $R^4$  are hydrogen, methyl or 1,8-naphthylidene.

507. The process as recited in claim 502 carried out at a temperature of about 25°C to about 100°C.

508. The process as recited in claim 502 wherein a partial pressure of said ethylene is about atmospheric pressure to about 275 MPa.

509. The process as recited in claim 502 wherein  $R^2$  and  $R^5$  are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and  $R^3$  and  $R^4$  are each independently hydrogen, hydrocarbyl, or  $R^3$  and  $R^4$  taken together are hydrocarbylene to form a ring.

510. A polymer blend comprising the polymer of claim 345, 349, 353, 354, 355, 358, 360 or 361 and one other polymer.

511. A nonwoven fabric wherein at least some fibers comprise the polymer of claim 345, 349, 353, 354, 355, 358, 360 or 361.

512. A shaped part comprising the polymer of claim 345, 349, 353, 354, 355, 358, 360 or 361.

513. A sheet or film comprising the polymer of claim 345, 349, 353, 354, 355, 358, 360 or 361.

514. A nonwoven fabric or microfiber comprising the polymer of claim 345, 349, 353, 354, 355, 358, 360 or 361.

515. A laminate wherein one or more of the layers comprises the polymer of claim 345, 349, 353, 354, 355, 358, 360 or 361.

516. The laminate as recited in claim 511 wherein a barrier layer is present.

517. A fiber comprising the polymer of claim 345, 349, 353, 354, 355, 358, 360 or 361.

518. A foam or foamed object comprising the polymer of claim 345, 349, 353, 354, 355, 358, 360 or 361.

519. A microporous membrane comprising the polymer of claim 345, 349, 353, 354, 355, 358, 360 or 361.

520. The polymer of claim 345, 349, 353, 354, 355, 358, 360 or 361 which is crosslinked.

521. The polymer of claim 345, 349, 353, 354, or 355 which is heat treated.

522. The polymer as recited in claim 521 which has 20 percent or more crystallinity.

523. A composition comprising the polymer of claim 345, 349, 353, 354, 355, 358, 360 or 361 and a nucleating agent.

524. A composition comprising the polymer of claim 345, 349, 353, 354, 355, 358, 360 or 361 and a flame retardant.

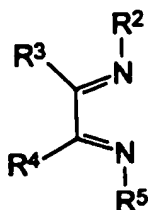
525. A composition comprising the polymer of claim 345, 349, 353, 354, 355, 358, 360 or 361 and an antioxidant.

526. A composition comprising the polymer of claim 345, 349, 353, 354, 355, 358, 360 or 361 and a filler or reinforcer.

527. A composition comprising the polymer of claim 345, 349, 353, 354, 355, 358, 360 or 361 which is electrically conductive.

528. A process, comprising, contacting, at a temperature of about  $-80^{\circ}\text{C}$  to about  $+20^{\circ}\text{C}$ , a compound of the formula  $(\eta^4\text{-1,5-COD})\text{PdMe}_2$ , and a diimine of the formula

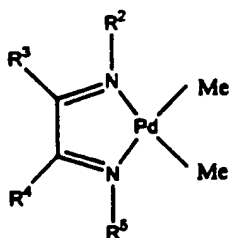
5



(VIII)

to produce a compound of the formula

10



(XXXXI)

wherein:

COD is 1,5-cyclooctadiene;

15

$\text{R}^2$  and  $\text{R}^5$  are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and

$\text{R}^3$  and  $\text{R}^4$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or  $\text{R}^3$  and  $\text{R}^4$  taken together are hydrocarbylene or substituted hydrocarbylene to form a ring.

20

529. The process as recited in claim 528 wherein said temperature is about  $-50^{\circ}\text{C}$  to about  $+10^{\circ}\text{C}$ .

25

530. The process as recited in claim 528 wherein  $\text{R}^2$  and  $\text{R}^5$  are both 2-*t*-butylphenyl or 2,5-di-*t*-butylphenyl, and  $\text{R}^3$  and  $\text{R}^4$  taken together are 1,8-

naphthyllylene, or R<sup>3</sup> and R<sup>4</sup> are both hydrogen or methyl.

531. The process as recited in claim 528 wherein R<sup>2</sup> and R<sup>5</sup> are each independently hydrocarbyl, provided  
5 that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and R<sup>3</sup> and R<sup>4</sup> are each independently hydrogen, hydrocarbyl, or R<sup>3</sup> and R<sup>4</sup> taken together are hydrocarbylene to form a ring.

10 532. The compound as recited in claim 232, 248, 253, 259, 267, 317, 334, 339, 461 or 466 wherein X is part of a heterogeneous support.

533. The compound as recited in claim 532 wherein said heterogeneous support is montmorillonite.

15 534. The process as recited in claim 49, 97, 176, 199, 280, 299, 451, 452 or 482 wherein X is part of a heterogeneous support.

535. The process as recited in claim 49, 97, 176, 199, 280, 299, 451, 452 or 482 wherein a polymerization  
20 catalyst is supported on a heterogeneous support.

536. The compound as recited in claim 232, 248, 253, 259, 267, 317, 334, 339, 461 or 466 which is supported on a heterogeneous support.

537. The process as recited in claim 49, 97, 176,  
25 199, 280, 299, 451, 452 or 482 wherein the polymerization is run in the gas phase.

538. The process as recited in claim 478 which is run in a fluidized bed reactor.

539. A flexible pouch made from a single or  
30 multilayer film which comprises the polymer of claim 1, 3, 4, 6, 7, 332 or 343.

540. The polymer of claim 1, 3, 4, 6, 332 or 343 grafted with a compound containing ethylenic unsaturation and a functional group.

35 541. The polymer as recited in claim 540 wherein said functional group is carboxyl, carboxylic anhydride, ester or a carboxylate salt.

542. A wrap packaging film having differential  
cling, comprising a film laminate having at least two  
layers;

an outer reverse layer which comprises a  
5 polymer of claim 1, 3, 4, 6, 7, 332 or 343, and a  
tackifier present in sufficient amount to impart cling  
properties; and

an outer obverse layer which has a density of  
at least about 0.916 g/mL and which has little or no  
10 cling; and

provided that a density of said outer reverse  
layer is at least 0.008 g/mL less than that of a  
density of said outer obverse layer.

543. A fine denier fiber comprising the polymer of  
15 claim 1, 3, 4, 6, 7, 332 or 343.

544. A composition, comprising, a polymer of claim  
1, 3, 4, 6, 7, 332 or 343 and an antifogging agent.

545. The process as recited in claim 13, 15 or 142  
wherein said bidentate ligand or second compound is  
20 (XXX) and  $n$  is 2, all of  $R^{30}$ ,  $R^{28}$  and  $R^{29}$  are hydrogen,  
and both of  $R^{44}$  and  $R^{45}$  are 9-anthracenyl.

546. The process as recited in claim 65 or 84  
wherein said compound or said second compound is (XVII)  
and  $n$  is 2, all of  $R^{30}$ ,  $R^{28}$  and  $R^{29}$  are hydrogen, and  
25 both of  $R^{44}$  and  $R^{45}$  are 9-anthracenyl.

547. The process as recited in claim 65 or 84  
wherein said compound or said second compound is (XVII)  
and  $n$  is 2, all of  $R^{30}$ ,  $R^{28}$  and  $R^{29}$  are hydrogen, both of  
 $R^{44}$  and  $R^{45}$  are 9-anthracenyl,  $M$  is Ni, and  $n$  is 2.  
30

548. The compound or process as recited in claim  
299 or 317 wherein  $M$  is Ni or Pd and  $m$  is 2.

549. The process as recited in claim 299 wherein  $M$   
is Ni.

550. The process as recited in claim 49 wherein  
35 said olefin comprises cyclopentene.

551. The process as recited in claim 65 wherein  
said olefin comprises cyclopentene.



552. The process as recited in claim 452 wherein said olefin comprises cyclopentene.

553. The process as recited in claim 548 wherein said monomer comprises cyclopentene.

5 554. The process as recited in claim 17, 48, 124, 151, 156, 167, 180, 231, 298, 316, 550, 551, 552 or 553 wherein cyclopentene is a solvent.

555. The process as recited in claim 37 wherein:

10  $R^2$  and  $R^5$  are both 2,4,6-trimethylphenyl or 2,6-dimethylphenyl;

$R^3$  and  $R^4$  taken together are 1,8-naphthylidene;

y and z are both 1;

M is Ni;

Q and S are both chloride, iodide or bromide;

15 and

m is 2.

556. The process as recited in claim 555 wherein said first compound is an alkylaluminum compound.

20 557. The process as recited in claim 556 wherein said alkylaluminum compound is ethylaluminum dichloride or methylaluminoxane.

558. The process as recited in claim 555, 556 or 557 wherein said monomer comprises cyclopentene.

25 559. The process as recited in claim 558 wherein cyclopentene is a solvent.

560. The polymer as recited in claim 1, 3, 4, 6, 332 or 343 which has:

a melt flow ratio,  $I10/I2 \geq 5.63$ ;

30 by the equation:  $Mw/Mn \leq (I10/I2) - 4.63$ ; and

a critical shear rate at onset of surface melt fracture of at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear olefin polymer having about the same I2 and Mw/Mn.

35

561. A composition comprising:

the polymer as recited in claim 1, 3, 4, 6, 332 or 343 which has:

- a melt flow ratio,  $I_{10}/I_2$ ,  $>$  or  $= 5.63$ ;
- a molecular weight distribution,  $M_w/M_n$ , defined by the equation:  $M_w/M_n < OR = (I_{10}/I_2) - 4.63$ ; and
- a critical shear rate at onset of surface melt
- 5 fracture of at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear olefin polymer having about the same  $I_2$  and  $M_w/M_n$ ; and
- at least one other: natural polymer; a synthetic
- 10 polymer chosen from the polymer of claims 1, 3, 4, 6, 332, or 343; or a conventional high density polyethylene, low density polyethylene or linear low density polyethylene polymer.
562. The polymer as recited in claim 1, 3, 4, 6,
- 15 332, 343, 383, 384, 385, 386 or 387 which has a melt flow ratio,  $I_{10}/I_2 \geq 5.63$ , a molecular weight distribution,  $M_w/M_n$ , defined by the equation:  $M_w/M_n \leq (I_{10}/I_2) - 4.63$ , and a critical shear stress at onset of gross melt fracture of greater than about 400 kPa.

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☒ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**